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The Effects of Liquid Nitrogen on Concrete Hydration, Microstructure and Properties

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The Effects of Liquid Nitrogen on Concrete Hydration, Microstructure, and Properties

by

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Dedication

To my wife and kids who gave me the staying power to see this through until the end.

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The Effects of Liquid Nitrogen on Concrete Hydration, Microstructure and Properties

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Controlling the placement and hydration temperature of concrete is important to concrete durability. Thermal gradients and delayed ettringite formation (DEF) result in cracking when concrete in the plastic state becomes too hot. Cooler placement temperatures slow hydration reaction, increase working time, reduce the maximum temperature in the concrete member, and reduce thermal gradients. Furthermore, cooler concrete achieves better long-term strength and microstructural development. Concrete producers have been using multiple methods of reducing the placement temperature of concrete, such as cooling mixtures with ice or chilled water, shading aggregate piles, placing concrete at night, and using evaporative cooling of aggregate piles. More recently, concrete producers have turned to liquid nitrogen for cooling fresh concrete. The objective of this research was to determine the effects of liquid nitrogen on concrete hydration, microstructural development, and performance. The following concrete mixture properties and methods were investigated: cement type, the effects of selected supplementary cementing materials and chemical admixtures, placement temperature,

and the time at which liquid nitrogen dosing occurs (delayed dosing). Concrete performance was tested in terms of slump, setting time, yield, compressive and splitting tensile strength, elastic modulus, rapid chloride permeability, and hardened and fresh air void analysis. Hydration and microstructural development were monitored by isothermal calorimetry, semi-adiabatic calorimetry, x-ray diffractometry, inductively coupled plasma, and environmental scanning electron microscopy. Additional testing was performed on concrete mixing drums to determine the effects of liquid nitrogen on the durability of steel mixing drums. The results indicate that performance, hydration, and microstructural development of fresh concrete are relatively unaffected when cooled with liquid nitrogen to room temperatures. Significant findings show that the slump of liquid nitrogen cooled concrete is similar to hot concrete mixtures and not room temperature mixtures. Additionally, setting time results show that liquid nitrogen dosing of hot concrete can be delayed for up to 1 hour and setting times will still be similar to room temperature mixtures. Based on findings from this research study, liquid nitrogen is recommended as a primary cooling option to reduce the placement temperature of fresh concrete.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1: INTRODUCTION

1.1 PROBLEM STATEMENT

It is common practice to cool concrete during hot weather or for mass placements. In hot weather conditions, solar radiation and elevated temperatures preheat concrete mixing materials and the drums of ready-mix trucks, increasing the placement temperature of the concrete. Furthermore, a combination of extreme temperatures, low relative humidity, and wind may result in conditions that are adverse to the placement and finishing of concrete. Since cement hydration reactions are accelerated by higher temperatures and are exothermic, the rate at which heat is produced is therefore accelerated, further increasing the temperature of the concrete. This cyclical development of heat produces a "self-stoking" process causing hydration reactions to accelerate and the concrete to become hotter. This will certainly result in a reduced working time for the fresh concrete, and may also cause other problems as discussed next.

Temperature related issues are particularly a problem with mass concrete placements. In relatively small structural elements, the heat produced by cement hydration is easily dissipated to the surrounding environment because of the large surface-to-volume ratio. However, in mass concrete, the surface-to-volume ratio is smaller, thereby restricting the amount of heat loss into the environment. The insulating effects of the surrounding concrete cause thermal gradients between the hot interior and the colder exterior surface (Fig. 1.1). The hot interior of these structural elements will have a larger thermal expansion than the cooler exterior. This mismatch in thermal expansion may result in thermal cracking if the difference in strain between two adjoining regions exceeds the tensile strain capacity of the concrete. Furthermore, restricted heat dissipation near the core of concrete elements may result in excessively high temperatures, which may increase the susceptibility of the concrete to delayed ettringite formation (DEF) and lead to future durability related problems.

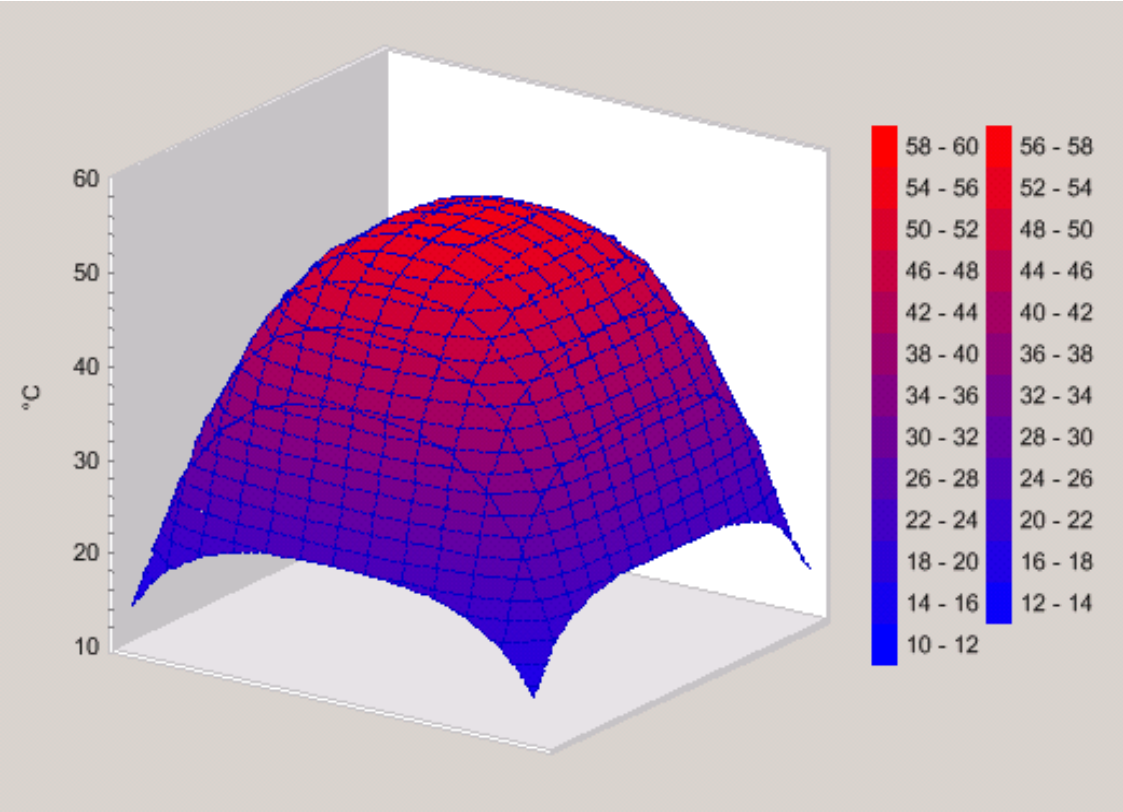


FIGURE 1.1 Example of the temperature distribution in a horizontal cross section of an 8' by 10' column at 24 hours (image courtesy of Kyle Riding, The University of Texas at Austin)

Reducing the placement temperature of concrete can result in many improvements. Cooler starting temperatures slow the hydration reactions, increase working time, reduce the maximum temperature in the concrete member, and reduce thermal gradients. Furthermore, cooler concrete achieves better long-term strength and microstructural development. Concrete suppliers have been using multiple methods of reducing the placement temperature of concrete, such as cooling the mixtures with ice or chilled water, shading the aggregate piles, placing concrete at night, and using evaporative cooling of aggregate piles.

More recently, concrete producers have turned to liquid nitrogen (LN) for cooling fresh concrete. The effects of this cooling method on concrete hydration, microstructural development, and performance have not been investigated. Since the process of cooling

with LN is very different from the more traditional methods, it is not known whether or not LN can impact hydration, concrete performance, and durability in more ways than are simply achieved by the reduction in temperature alone. Furthermore, the interactions between LN cooling and the mechanisms of chemical admixtures (e.g. water reducers and air-entraining agents) are unknown. Additionally, LN presents the opportunity to change the temperature of the concrete at any time during mixing, allowing for delayed cooling. This cannot be achieved with the other cooling methods, and the effects of delayed cooling on the hydration and resulting properties have never been investigated. The research presented in this dissertation addresses these questions.

1.2 ORGANIZATION OF DISSERTATION

Results from this research provide insights into the effects of LN on cement hydration and concrete properties. First, in Chapter 2, background information is presented, providing details about the temperature-related problems in mass concrete, concrete cooling methods, potential problems arising from the use of LN to cool concrete, and a review of previous relevant work. Experimental results are presented next in Chapter 3, beginning with the effects of LN on fresh concrete properties determined through flow testing on cement mortar and slump, setting time, and yield (unit weight) testing of fresh concrete. In Chapter 4, the effects of LN on hardened concrete properties are discussed, including compressive strength testing of hardened mortar and compressive strength, splitting tensile strength, elastic modulus, and rapid chloride ion permeability testing on hardened concrete. Since cement hydration is directly affected by temperature, a series of analytical methods were employed and are discussed in Chapter 5, including isothermal and semi-adiabatic calorimetry, X-ray diffraction (XRD), inductively coupled plasma (ICP), and environmental scanning electron microscopy (ESEM). Based on the results from analytical testing, additional analyses were performed on the effects of delaying the time of LN application into the concrete mixture to determine the subsequent effects on setting time and compressive strength; these are discussed in Chapter 6. Testing was also performed to determine the effects of LN application on the fresh and hardened air content of concrete, presented in

Chapter 7. The extreme temperature of LN necessitated a study concerning the effects of cryogenic temperatures on steel mixing drums. Temperature readings of steel mixing drums were recorded during LN injection and a chemical analysis was performed on steel from fractured mixing drums; these results are reported in Chapter 8. Conclusions and future work are discussed in Chapter 9.

CHAPTER 2: BACKGROUND

2.1 INTRODUCTION

Concrete is the most widely used construction material in the world. The raw materials that comprise concrete can be easily found in most parts of the world, making concrete a relatively inexpensive building material in comparison to other materials. Material quality and proper curing have a direct and significant impact on long-term concrete durability. In particular, the internal temperature of curing concrete needs to be controlled to ensure proper hydration. This chapter addresses the effects of temperature on concrete properties and provides a historical perspective on temperature related issues with fresh concrete, particularly in mass concrete. In addition, this chapter discusses the adverse effects of high curing temperatures (delayed ettringite formation and thermal cracking) and presents methods of controlling the development of high temperatures in fresh concrete (placement temperature, scheduling, cooling ingredients, and liquid nitrogen). The significance of this research is also presented.

2.2 TEMPERATURE EFFECTS ON CONCRETE PROPERTIES

Cement hydration is a chemical process that is directly affected by temperature. Elevated curing temperatures increase cement hydration, resulting in high early strengths. At later ages, however, the strength of concrete hydrated at elevated temperatures is lower in comparison to that hydrated at ambient temperature (Price, 1951). During the cement hydration process, rims of hydration product form around the outer perimeter of cement grains. The rims form as cement grains are solublized and individual ions migrate out of the cement grain; the ions precipitate on the outer edge of the cement grain and form rim-like layers of hydration products. The formation of these hydration products accelerates with temperature and is responsible for high early strength development. Rapid hydration leads to a more heterogeneous distribution of hydration products resulting in a coarser porosity in the cement matrix and an increase in the mean

pore radius (Escalante-Garcia and Sharp, 1998). Higher curing temperatures cause diffusing ions to react faster than they can diffuse, causing hydrates to precipitate more around cement grains and form a thicker shell around them (Kjellsen and Detwiler, 1992). The dense rims around the cement grains further reduce the diffusion of ions and consequently slow down hydration. Under normal (room temperature) conditions, hydration occurs slowly and allows ions to diffuse more uniformly throughout the cement matrix before the ions precipitate. This leads to a less dense calcium silicate hydrate (C-S-H) layer around cement grains and a homogeneous distribution of hydration products, which results in lower coarse porosity and smaller pores (Komonen and Penttala, 2003).

Concrete properties such as strength, setting time, and workability (slump) are sensitive to temperature. Elevated curing temperatures increase strength at early ages, decrease setting times, and reduce workability (Burg, 1996). High curing temperatures cause an increase in strength since the microstructure is more homogeneous (Mindess et al., 2003). Strength is reduced, however, at later ages. Several sources confirm that cement hydration decreases at later ages for samples cured at elevated temperatures thereby reducing strength gain (Idorn, 1969). On the other hand, samples cured at cooler temperatures actually have a higher degree of reaction which results in increased strengths at later ages.

The effect of temperature on initial set and workability is in direct relationship to microstructural development. Low curing temperatures slow hydration and increase setting times and workability. Conversely, elevated curing temperatures increase hydration and decrease setting times and workability. Recent research has shown that a 30% decrease in setting time can be expected for each 10°F increase from ambient temperature (Burg, 1996). This can cause significant problems with respect to workability. Results from the same study has, also, shown that that slump will decrease approximately 0.8-inch for each 20°F increase from ambient temperature (Burg, 1996).

Concrete cured at lower temperatures provide many benefits to concrete properties and microstructure. Cement microstructure develops more uniformly and allows for greater strength gains at later ages. Similarly, setting times increase and workability is improved.

2.3 MASS CONCRETE

The sensitivity of concrete to thermally-related durability problems has long been recognized by the research community, engineers, and state and federal highway agencies. Dam engineers are especially cognizant of the thermal effects of concrete since the potential for elevated temperatures and large thermal gradients in dams is high and the tolerance for cracking is extremely low. State departments of transportation possess many structures that can be considered critical massive structures, such as footings, bridge columns, and bent caps. Therefore, many agencies have adopted guidelines to minimize the effects of temperature on mass concrete. In 1930, the American Concrete Institute (ACI) established a committee to develop guidelines in response to the rapid pace of dam construction during that era and to satisfy questions regarding thermal cracking (ACI 207, 1996).

In current ACI documents, mass concrete is vaguely defined as "any volume of concrete with dimensions large enough to require that measures be taken to cope with generation of heat from hydration of the cement and attendant volume change, to minimize cracking" (ACI 116, 2000). Therefore, engineers, owners, and government agencies responsible for a mass placement must clearly establish their own guidelines that account for various factors. Some of these factors are identified in section 8 of ACI 301, "Specifications for Structural Concrete," which states (ACI 301, 1999):

> Designate portions of the structure to be treated as either plain mass concrete or reinforced mass concrete. Whether or not concrete should be designated as mass concrete depends on many factors such as weather conditions, the volume-surface ratio, rate of hydration, degree of restraint to volume change, temperature and mass of surrounding materials, and functional and aesthetic effect of cracking. In general, heat generation should be considered when the minimum cross-sectional dimension approaches or exceeds 2-1/2 ft [760 mm] or when cement contents above 600 lb/yd^3 [356 kg/m^3] are used. The requirements for each project, however, should be evaluated on their own merits.

The Texas Department of Transportation (TxDOT) defines mass concrete as placements with a least dimension greater than or equal to 5 feet (TxDOT 420.4, 2004). A research study conducted at the University of Florida identified 17 state departments of transportation (DOT) that have a mass concrete specification or make special provisions for mass placements (Chini et al., 2003). A review of each state's mass concrete specifications revealed significant variations in defining the least dimension. For example, the smallest dimension was specified by Idaho DOT as 3.93 ft. for a footing and the largest dimension was given by California DOT at 6.56 ft. (Chini et al., 2003).

Once concrete is identified as being mass concrete, preventive measures should be conducted to avoid large thermal gradients, excessive internal temperatures, and extreme temperature differentials. In TxDOT specification 420.4.14, the following procedures are given for mass concrete (TxDOT 420, 2004):

> For monolithic mass placements, develop and obtain approval for a plan to ensure the following during the heat dissipation period:
>
> - the temperature differential between the central core of the placement and the exposed concrete surface does not exceed 35°F (19.4°C) and
> - the temperature at the central core of the placement does not exceed 160°F (71.1°C)
>
> Base this plan on the equations in the Portland Cement Association's *Design and Control of Concrete Mixtures*. Cease all mass placement operations and revise the plan as necessary if either of the above limitations is exceeded.
>
> Include a combination of the following elements in this plan:
>
> - selection of concrete ingredients including aggregates, gradation, and cement types, to minimize heat of hydration;
> - use of ice or other concrete cooling ingredients;
> - use of LN dosing systems;
> - controlling rate of time of concrete placement;

- use of insulation or supplemental external heat to control heat loss;
- use of supplementary cementing materials; or
- use of a cooling system to control the core temperature.

> Furnish and install 2 sets of temperature recording devices, maturity meters, or other approved equivalent devices at designated locations. Use these devices to simultaneously measure the temperature of the concrete at the core and the surface. Maintain temperature control methods for 4 days unless otherwise approved.

Other transportation agencies have similar temperature requirements, although they vary slightly. Most states have a maximum temperature differential between 27°F and 50°F (15°C and 27.8°C), a maximum placement temperature between 65°F and 80°F (18.3°C and 26.7°C), and a maximum curing temperature between 160°F and 176°F (71.1°C and 80°C) (Chini et al., 2003). Compliance with the maximum temperature differential significantly reduces the risk of thermal cracking by maintaining a smaller temperature gradient throughout the mass placement. Therefore, there will be less restraint from the hotter concrete core when the colder exterior surface contracts. Additionally, compliance with the maximum curing temperature reduces the risk of delayed ettringite formation (DEF) since the temperature threshold at which DEF occurs is approximately 160°F (71.1°C). However, placement temperature and maximum curing temperature are not mutually exclusive. In order to maintain the maximum curing temperature below the DEF threshold, the placement temperature must be within a specified range.

2.4 DELAYED ETTRINGITE FORMATION (DEF)

Ettringite is a crystal that develops in normal cement hydration reactions and will grow where space permits its formation, such as in air voids, capillary pores, or in cracks. Ettringite formation will not cause cracking as long as the concrete is still in a plastic state during its development or if it grows in empty spaces, such as air voids. However,

since the late 1980s, researchers have discovered a phenomenon known as delayed ettringite formation that occurs during high-temperature curing.

DEF is a chemical process in concrete that affects durability and may lead to expansion and subsequent cracking. Concrete in which temperatures exceeded 158°F (70°C) during initial curing is most susceptible to DEF. The source of heat may be supplied externally, in the case of precast operations, or it may be caused by cement hydration reactions, especially in mass concrete elements or during hot weather concreting. As cement grains dissolve in water and begin to form initial hydration products, sulfates become trapped in rapidly forming C-S-H. Once the concrete has hardened, the trapped sulfates are released into the concrete matrix and react with other hydration products to form ettringite (Hall, 2003). This late ettringite causes expansion on the paste and subsequent cracking in the concrete.

DEF is linked to significant cracking and loss of serviceability in affected structures. The most effective method in reducing the susceptibility of DEF is to limit the maximum concrete temperature during initial curing to below 149 – 158°F (65 – 70 °C). As stated in the previous section, most transportation agencies have adopted maximum curing temperature specifications in response to this problem.

2.5 THERMAL CRACKING

Heat generated during cement hydration reactions may have a profound effect on concrete durability. In mass concrete, the increase in concrete temperature during curing results from the heat of hydration of cementitious materials and the insulating effects of the surrounding concrete. The interior concrete increases in temperature and expands while the surface concrete may be cooling and contracting. Large differences between ambient and internal temperatures may result in thermal cracking if the thermal tensile stresses exceed the tensile strength of the early-age concrete. The severity of cracking is a function of the temperature differential, concrete properties, and the amount of reinforcing steel (PCA IS177, 2001). Transportation agencies have established maximum temperature differentials between 27°F and 50°F (15°C and 27.8°C) to decrease the risk for thermal cracking in large structural elements (Chini et al., 2003).

2.6 CONCRETE PLACEMENT TEMPERATURE

The placement temperature of concrete has a significant effect on the susceptibility to thermal cracking and DEF. The exothermic reactions of cement hydration produce heat that gradually increases the concrete temperature. The most effective way to ensure that the cement hydration reactions do not cause the concrete to exceed temperature specifications is to reduce the placement temperature of the concrete. Figure 2.1 shows examples of temperature distributions 24 hours after placement in 7ft. by 7ft. columns with identical mixture designs and formwork conditions. Figure 2.2 shows the temperature development versus time for the same columns.

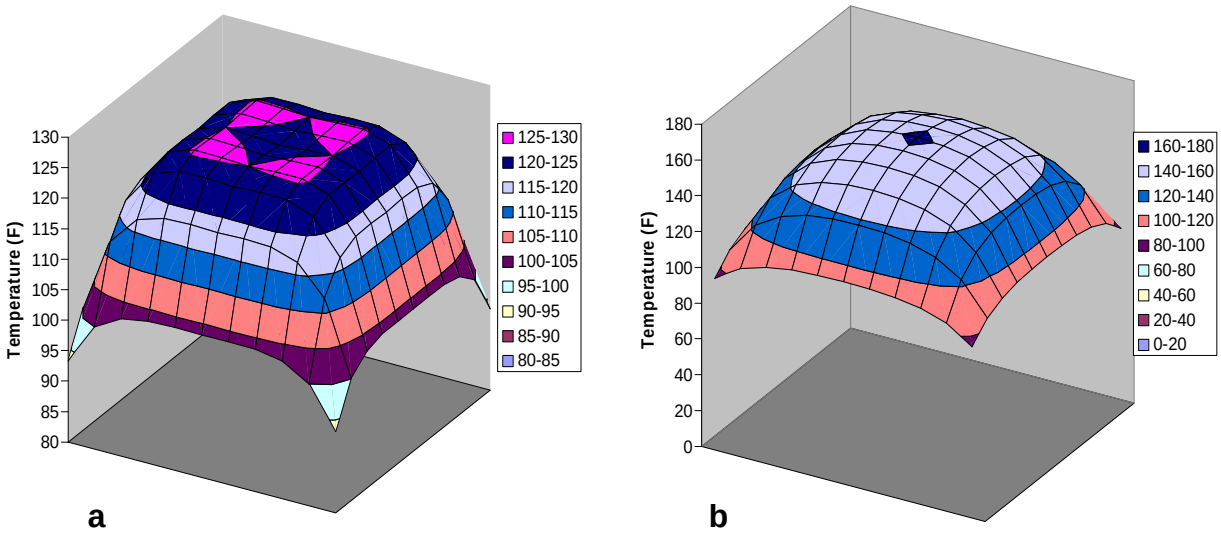


FIGURE 2.1 Examples of the temperature distribution in a horizontal cross section of a 7ft. by 7ft. column at 24 hours, (a) 75°F (23.9°C) placement temperature, (b) 95°F (35°C) placement temperature (image courtesy of Kyle Riding, The University of Texas at Austin)

The column with the 75°F (23.9°C) placement temperature in Figure 2.1a and Figure 2.2a meets TxDOT's specification for maximum curing temperature (~130°F, 54.4°C) and maximum temperature differential (~35°F, 19.4°C). The column placed with a 95°F (35°C) temperature in Figure 2.1b and 2.2b clearly exceeds the temperature

specification for both maximum curing temperature (~160°F, 71.1°C) and maximum temperature differential (~60°F, 33.3°C). TxDOT's temperature specification would not allow the condition Fig. 2.1b and 2.2b because it sets the minimum concrete placement temperature at 50°F (10°C) and maximum concrete placement temperatures at 95°F (35°C) for pavements, 85°F (29.4°C) for bridge decks, and 75°F (23.9°C) for mass placements (TxDOT 420, 2004).

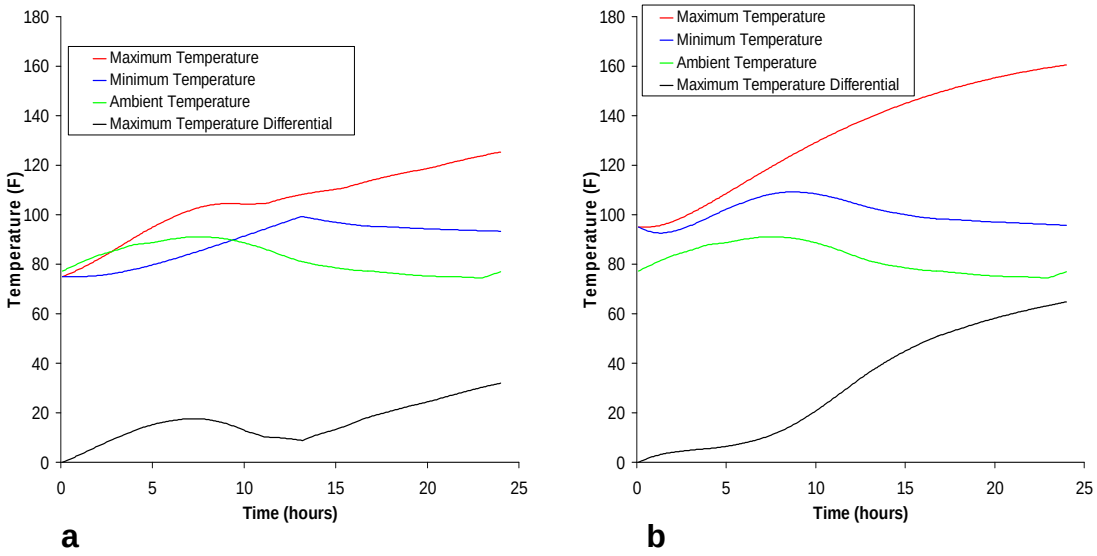


FIGURE 2.2 Temperature profiles over time of the columns shown in Figure 2.1, (a) 75°F (23.9°C) placement temperature, (b) 95°F (35°C) placement temperature

The process of achieving a placement temperature of 75°F (23.9°C) for mass pours is quite difficult, especially in warm climates and during the summer months. Often, concrete mixing materials, especially aggregate, and the drums of ready-mix trucks are not shaded from the sun and are very hot. In combination, these factors make it very difficult to keep the placement temperature within specification guidelines. However, several cooling methods exist to provide cool concrete under hot conditions, such as scheduling, cooling concrete ingredients, or injecting LN into the mixture.

2.7 SCHEDULING

For decades, contractors have used scheduling to control temperature rise in fresh concrete. For mass concrete pours, contractors would usually wait until the early evening or night before placing concrete so they could avoid the hottest part of the day. By doing this, contractors could ensure that the peak temperature in the concrete would occur at night when the air temperature is the coolest. In addition, contractors could avoid heating due to solar radiation and hot air temperature.

However, most construction projects no longer have the option of pouring concrete only at night. Large roadway projects are on a fast-track schedule that requires pouring concrete 24 hours a day. Limiting concrete pours specifically to night hours would double the amount of time required to complete a project, thereby increasing the cost of the project and perhaps negatively affecting public opinion. Therefore, scheduling only at night is not a viable option unless project timelines allow for it.

2.8 COOLING CONCRETE INGREDIENTS

One common method of lowering the placement temperature of concrete is to cool the concrete ingredients. Specifically, attempts have been made to cool the aggregate and water before it enters the central mixer. Since aggregate comprises approximately 70% of a concrete mixture, it is therefore critical to keep the temperature of the aggregate as low as possible. The amount of heat that an ingredient contributes to a concrete mixture is a function of the quantity of an ingredient and its specific heat. Mindess et al. (2003) provide an equation to calculate the temperature of concrete based on individual constituents:

$$T = \frac{0.22(T_a M_a + T_c M_c) + T_w M_w + T_{wa} M_{wa}}{0.22(M_a + M_c) + M_w + M_{wa}} \qquad \text{Equation 2-1}$$

where T is the temperature of the fresh concrete (°C); T_a, T_c, T_w, and T_{wa} are the temperatures of the aggregates, cement, mixing water, and free water on aggregates, respectively, and M_a, M_c, M_w, and M_{wa} are their individual masses (kg).

2.8.1 Aggregates

Aggregates are the largest constituents of concrete and have a significant effect on fresh concrete temperature. In warm weather environments and hot summer months, it is difficult to keep aggregates cool since they are typically deposited in the ready-mix yard and left fully exposed to the sun. One common cooling method is to wet the aggregate piles so that they cool by evaporation. An advantage of this method is that wet piles actually have more uniform moisture contents than dry piles (Lee, 1989). The best temperature reduction of concrete that can be expected by evaporative cooling of aggregates is only 6°F (3.3°C) (Malisch, 1997).

Research has been conducted in Japan investigating the effects of freezing sand piles with LN to increase the cooling potential of fresh concrete. Unfrozen sand with temperatures ranging from 72 to 87°F (22.2 to 30.6°C) was compared to sand frozen with LN to temperatures of 30 to -220°F (-1.1 to -140°C). Using frozen sand at -220°F (-140°C), the temperature of some concrete mixtures were reduced by 77°F (25°C) (Kurita et al., 1990). However, a special sand cooling apparatus was needed to agitate the sand with mixing blades so that the sand particles did not clump together when cooled. The research did not address potential problems that occur when stationary sand piles become wet due to precipitation, high humidity, or intentional saturation. Cooling wet sand piles with LN causes the sand particles to agglomerate. If the mixing action of the central mixer or the ready-mix truck is not adequate, the sand will not disperse adequately in the concrete mixture, thereby creating weak zones in the hardened concrete.

2.8.2 Water

The means by which water is cooled or kept cool are relatively simple. Water can be cooled by limiting sun exposure of storage tanks, burying supply pipes, and by using an industrial chiller. The best temperature reduction that can be expected in a concrete mixture by chilling water is only 5°F (2.8°C) (Malisch, 1997).

A very popular method of cooling concrete is to replace some or all of the mixing water with ice. Ice is typically provided in bags and must be flaked or crushed before being manually loaded into the mixing truck. An advantage to this method is that much

cooler temperatures can be achieved than with chilling water. Ice provides more cooling than chilled water because of the additional power provided from the heat of fusion. Another advantage is that minimal equipment is needed and ice-cooling can be done on a short-term basis or on very little notice, without high associated costs. The fresh concrete temperature when using ice can be estimated by modifying equation 2-1 to be as follows (Mindess et al., 2003):

$$T = \frac{0.22(T_a M_a + T_c M_c) + T_w M_w + T_{wa} M_{wa} - 76.6°C M_i}{0.22(M_a + M_c) + M_w + M_{wa} + M_i} \qquad \text{Equation 2-2}$$

where M_i is the mass of ice (kg). When ice replaces only half of the mixing water, concrete can be cooled by 12°F to 20°F (6.7°C to 11.1°C) (Malisch, 1997).

2.8.3 Cement

The temperature of cement has a minimal effect on fresh concrete temperature. The most significant factor that affects cement temperature is sun exposure. Although very little can be done to cool cement, the best possible way to keep cement cool is to limit sun exposure of the cement storage silos. Cooling cement by 9°F (5°C) only reduces the fresh concrete temperature by 0.9°F (0.5°C) (Lerch, 1955). However, provisions must be taken to ensure that cement does not retain an excessive amount of heat from cement production. Therefore, ACI specifications limit the maximum cement temperature to 150°F – 180°F (65.6°C - 82.2°C) (ACI 305, 1999).

2.8.4 Limitations of Cooling Concrete Ingredients

Although cooling concrete ingredients is an effective means of lowering the fresh temperature of concrete, there are several limitations to the cooling procedures in terms of their efficacy, cost, and effects on concrete properties. In terms of cost, several of the methods employ large pieces of equipment that require an initial capital expenditure.

However, the expense may not be significant if the cost is divided per cubic yard for large volumes of concrete.

The largest disadvantage to cooling aggregates by evaporation is that it can only be performed in dry climates. Many of the warm weather climates around the world are relatively humid, thereby limiting this method to a few select regions or to specific conditions.

Chilled water is a common method of cooling concrete but has severe limitations in terms of cooling potential. Even if all of the mixing water is replaced with chilled water, the best temperature reduction that can be expected is only 5°F (2.7°C) (Malisch, 1997). In terms of cost, a 60,000 gallon water storage tank may cost more than $20,000 (Lee, 1989). An underground storage pit, however, may cost half of that (Lee, 1989). The cost to chill water depends on the initial temperature of the water but electricity in 1997 typically cost 4 to 12 cents per cubic yard (Malisch, 1997). Water sources such as wells or snow runoff springs require little to no chilling and would therefore cost very little to maintain the water at a low temperature. Based on cost alone, chilling water should only be considered if large volumes of concrete are required.

In spite of its popularity, cooling with ice has many disadvantages. Many man-hours are required to break bags of ice open, crush the ice, and add it into the mixing trucks. Unfortunately, no automated system exists to perform this simple task, and there is a high-injury rate associated with these jobs. Ice bags are manually dumped into crushers and workers occasionally are injured by becoming caught in the machinery. Furthermore, bagged ice is provided by the same ice manufacturers that supply ice to grocery stores, bars, restaurants, and other retail businesses. During specific times of the year, such as during the Super Bowl or doing a large local sporting event, there may be a premium on the cost of ice due to basic supply and demand concepts. Otherwise, ice manufacturers may simply run out of product, rendering the ready-mix plants inoperable until an alternative cooling method is found or until more ice is available.

A more significant problem is that it is difficult to difficult to ensure homogeneous distribution and complete melting. Ice cubes or flakes that do not completely melt are covered with mortar and are indistinguishable from similarly sized aggregate particles also covered with mortar. If the ice melts when the concrete has

already hardened, then large voids will be left in the concrete mass, thereby creating weak zones. Unmelted ice may also affect fresh concrete properties prior to setting by increasing the water-to-cement ratio in localized areas. Furthermore, it is very difficult to precisely control the temperature of fresh concrete when using ice. Cooling concrete mixtures to a specific temperature is a trial-and-error process that depends on the concrete volume, initial concrete temperature, outside temperature, relative humidity, and ice temperature. If the resulting concrete does not comply with the temperature specification, no additional ice may be added since it will increase the water content of the mixture.

2.9 LIQUID NITROGEN

Recently, concrete producers have turned to LN as a viable cooling method for fresh concrete. Typically, the concrete is cooled inside the ready-mix truck by direct injection of LN, which is maintained at a temperature of -320°F (-196°C) in a special storage tank that can endure cryogenic temperatures. In one of the most common systems, once the ready-mix trucks are charged with concrete, they drive under a simple frame and pull all the way through until the rear of the truck is aligned with the frame, as shown in Figure 2.3. The injection lance attached to the top of the frame is then activated and inserted into the rear of the mixing drum. As the drum spins at full speed, LN is injected into the mixture. For a relatively short time (milliseconds), the nitrogen is in liquid form but quickly turns to gas under normal atmospheric conditions. The nitrogen gas, however, is supercooled and has an extremely high cooling potential.

FIGURE 2.3 Cooling fresh concrete with liquid nitrogen

Although LN can be a dangerous material due to its extremely low temperature and high pressure, the injection operations are rather safe. Most LN injection systems are fully automated and are controlled by the batch operator from inside the control room, thereby adding an increased measure of safety. The simplicity of the process allows a single batch operator to successfully and safely perform both duties of charging mixing trucks and operating LN controls

The biggest advantage of the use of LN is that it allows for precise temperature control. The batch operator can use as much LN as is needed to achieve the desired temperature without having to make any adjustments to the water-to-cement ratio. Additionally, concrete can be chilled to even lower temperatures with LN than is possible

with ice or chilled water. In fact, liquid nitrogen cooled concrete (LNCC) can be cooled to near-freezing temperatures without affecting the workability significantly.

An alternative to cooling concrete directly in the ready-mix trucks is to cool it in the central mixer. The amount of cooling using this method, however, is limited to 3-5°F (1.7°C to 2.8°C) (Malisch, 1997). The remainder of the cooling is performed in the ready-mix trucks. An example of this procedure is given by Malisch as: 1.5 minutes of LN injection in a central mixer, then 2-7 minutes in the ready-mix truck depending on the initial concrete temperature (Malisch, 1997). One major disadvantage to this approach is the possibility of cracking the central mixer and rendering the ready-mix plant temporarily inoperable. If a mixing truck cracks, only one truck is removed from operation temporarily while the rest of the ready-mix plant operates at full capacity.

2.9.1 Concerns about Liquid Nitrogen

A significant concern when using LN is safety of the workers and of the equipment. The temperature of LN (-320°F,-196°C) is so low that prolonged exposure to skin may cause severe burns or frostbite. In more serious cases, LN can cause absolute freezing of body parts, resulting in amputation. The steel drums of ready-mix trucks are also sensitive to the extreme temperatures of LN. Most mixing drums are made of scrap steel that are durable enough to withstand abrasive stresses from concrete but not sufficient to endure thermal shock from LN. Steel undergoes a ductile-to-brittle transition at low temperatures, which increases the likelihood of cracking from thermal shock induced stresses. As the popularity of LNCC increases, specifications concerning dosing procedures must be established to ensure safety to humans and equipment.

Another concern is the cost associated with cooling concrete with LN. LN is a relatively unknown material in the construction industry, which makes cost data difficult to obtain. However, in 1997 Malisch reported that LN can cost between 30 – 55 cents for a 1°F (1.8°C) temperature reduction in a cubic yard of concrete (Malisch, 1997). The most costly part of a LN injection system is the specialized storage tank and cooling station. In addition, site preparation must be performed and a concrete slab must be built to support the massive storage tank. The costs of the storage tank, cooling stations, and

labor can exceed $20,000 – $60,000 per year (Malisch, 1997). However, in hot weather environments, the advantages may far outweigh the costs when considering the volume of concrete to be cooled and the required temperature reduction. In fact, LN may be the only option that will provide enough cooling for the concrete.

A significant concern with LN is the effect that it may have on concrete properties. Concrete that comes in contact with LN may freeze in localized areas and temporarily halt hydration in these locations. The course of cement hydration may be altered so that concrete will not develop strength optimally. Changes in hydration can also have implications on fresh properties such as slump and setting time, and hardened properties that are related to microstructure such as drying shrinkage and chemical durability.

Cement particles start to dissolve when mixed with water. Within the first few minutes of hydration, a layer of calcium silicate hydrate and ettringite form around cement grains to protect them from further immediate hydration. These initial hydration products are the reason for the induction period in concrete, a period of relative inactivity in concrete that allows for mixing and transport. Localized freezing with LN may interrupt these processes, with short-term or long-term implications on performance. For example, it is possible that LN may interfere with the initial formation of ettringite, a hydration product that prevents flash set in concrete and has long term durability implications, as discussed in Section 2.2.

Another concern is with the interaction of LN cooling with chemical admixtures. Many of these admixtures, such as high range water reducers and air-entraining admixtures, are sensitive to the time of addition and the temperature. LN dosing could interfere with the mechanisms of water reduction or air-entrainment.

2.10 PRIOR WORK

Nakane et al. (1992) researched the effects of LN on strength development and microstructure of cement paste. Three separate cooling methods were investigated in this research, which included air cooling materials before mixing, adding ice chips, and LN. Compressive strength testing showed no difference in the strength development of

cement pastes that were cooled to the same temperature with various cooling methods. Microstructural development was monitored by measuring pore volume and distribution and SEM imaging. Testing showed that regardless of the cooling medium, pore volume and distribution changed in almost the exact same manner. SEM imaging confirmed that LN had no effect on cement paste microstructure. Similarly, mixtures that were cooled to 32°F with LN were unaffected in terms of strength development and microstructure.

Nakahara et al. (1987) researched the use of LN to control temperature-related cracking in dam concrete. Slump, fresh air content, and compressive strength were measured to determine the effect that LN would have on these concrete properties. Research results showed no significant effect on concrete properties.

2.11 SIGNIFICANCE OF WORK

Very little research has been conducted on the effects of LN on concrete properties. Although the use of LN to cool fresh concrete has been performed for many years, comprehensive research has yet to be conducted to determine the effects that LN may have on concrete properties, hydration, and microstructural development. Results from this research will determine if there are any detrimental effects to injecting LN into fresh concrete and whether these results are reversible. The outcome of this research will establish criteria for the use of LN in fresh concrete.

CHAPTER 3: FRESH PROPERTIES OF MORTAR AND CONCRETE

3.1 INTRODUCTION

The fresh properties of concrete are greatly affected by concrete temperature. Concrete that is hot loses workability and experiences a higher rate of cement hydration, reducing setting time. To prevent these adverse affects, concrete needs to remain relatively cool during transport, placement, and hydration. In warm weather environments, keeping concrete cool is extremely difficult, especially during the summer months. Liquid nitrogen (LN) provides an abundance of cooling potential that allows concrete producers to cool concrete as cold as is necessary for the particular job. The use of LN allows for temperature reductions that could help concrete retain its workability and hydrate normally. To study the fresh properties of concrete, flow testing was conducted on cement mortars while slump, setting time and yield (unit weight) testing were conducted on concrete mixtures. The results from these tests are discussed in this chapter.

3.2 FRESH PROPERTIES OF HYDRAULIC MORTAR

Flow testing on mortar was performed according to ASTM C 1437, "Standard Test Method for Flow of Hydraulic Cement Mortar" (ASTM C 1437, 2001). Research on mortars was conducted as a "pilot" study in order to obtain quick results and to gain a basic understanding of the effects of LN on workability before making large concrete mixtures. Mortar testing allowed for multiple mixtures to be made on a single day. Furthermore, the small mortar mixtures expedited the research by narrowing down the concrete testing matrix and focusing the scope of the research.

3.2.1 Mortar Mixing Materials and Procedure

The materials used for the mortar consisted of TXI Type I/II cement from Hunter, Texas, manufactured sand from Austin Sand and Gravel in Southwest Austin, and

deionized water. The fine aggregate used in mortar testing was a limestone based river sand that was graded in accordance with ASTM C 33, "Standard Specification for Coarse Aggregate" (ACI C 33, 2003). The oxide analysis for the cement is shown in Table 3.1.

TABLE 3.1 Oxide Analysis for Type I/II Cement used in Mortar Mixtures

Name	Chemical Formula	Weight (%)
Silicon Dioxide	SiO_2	20.54
Aluminum Oxide	Al_2O_3	4.72
Iron Oxide	Fe_2O_3	3.17
Calcium Oxide	CaO	64.14
Magnesium Oxide	MgO	1.30
Sodium Oxide	Na_2O	0.12
Potassium Oxide	K_2O	0.38
Titanium Dioxide	TiO_2	0.20
Manganic Oxide	Mn_2O_3	0.41
Phosphorous Pentoxide	P_2O_5	0.06
Zinc Oxide	ZnO	0.02
Chromium Oxide	Cr_2O_3	0.12
Sulfur Trioxide	SO_3	2.88
Loss on Ignition		

Tricalcium Silicate	C_3S	60.55
Tricalcium Aluminate	C_3A	7.15
Dicalcium Silicate	C_2S	13.20
Tetracalcium Aluminoferrite	C_4AF	9.65

The proportions of materials for each mixture were comprised of one part cement to 2.75 parts of graded fine aggregate with a water-to-cement ratio of 0.485. Three test specimens from each mixture were evaluated for compressive strength at 1-, 3-, 7-, and 28-days, bringing the total number of test specimens for each mixture to twelve. ASTM C 109, “Standard Test Method for Compressive Strength of Hydraulic Cement Mortars,” provides proportioning data for the molding of six specimens, which was doubled for this

project in order to obtain the twelve necessary test specimens (ASTM C 109, 2005). The actual mixture proportions were as follows: 1.0 kg cement, 2.75 kg fine aggregate, and 242 mL water. Specimens were made using:

a. Ingredients at room temperature
b. Ingredients stored at 100°F and cooled to ~ 75°F using liquid nitrogen
c. Ingredients stored at 100°F and cooled to ~ 75°F using chilled water
d. Ingredients stored at 100°F and cooled to ~ 75°F using crushed ice

The admixtures used in the mortar mixtures consisted of two superplasticizers (Rheobuild 1000, BASF; and ADVA Flow, Grace), and two midrange water reducers (Pozzolith 961R and Pozzolith 200N, BASF). Admixture dosages were determined through the manufacturers' recommended dosage amounts.

Mortars were mechanically mixed in accordance with ASTM C 305, "Standard Practice for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency" (ASTM C 305, 1999). The paste was then tested for flow in accordance with ASTM C 1437.

3.2.2 Results of Flow Testing

Figures 3.1 to 3.5 present flow data for mortar mixtures in the test matrix. The flow is the resulting increase in average base diameter of the mortar mass, expressed as a percentage of the original base diameter. The graphs are categorized by admixture so that correlations could be made to determine if the method of cooling (liquid nitrogen, chilled water, or ice) affected the performance of the admixtures. ASTM specifies that the error for similar mixtures by the same operator is 11%, which is indicated by the error bars on each cooling method bar. The temperatures located within the bars indicate the final mortar temperature after cooling.

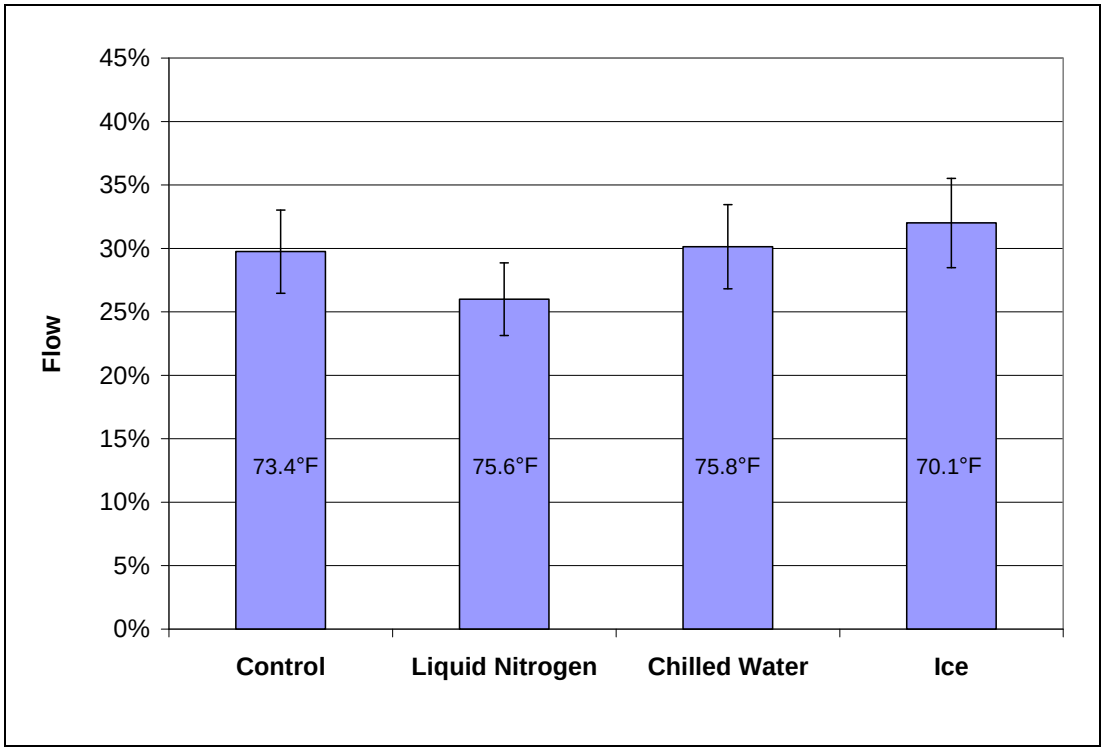


FIGURE 3.1 Flow of cement mortar containing no admixtures

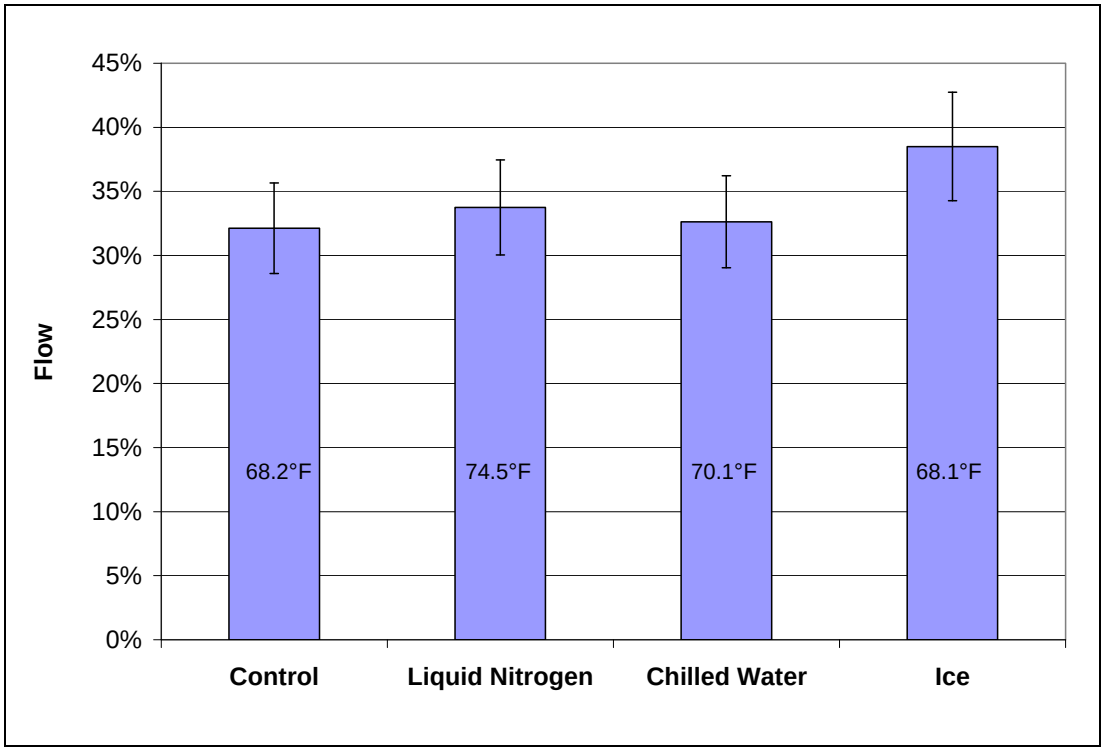


FIGURE 3.2 Flow of cement mortar containing Rheobuild 1000

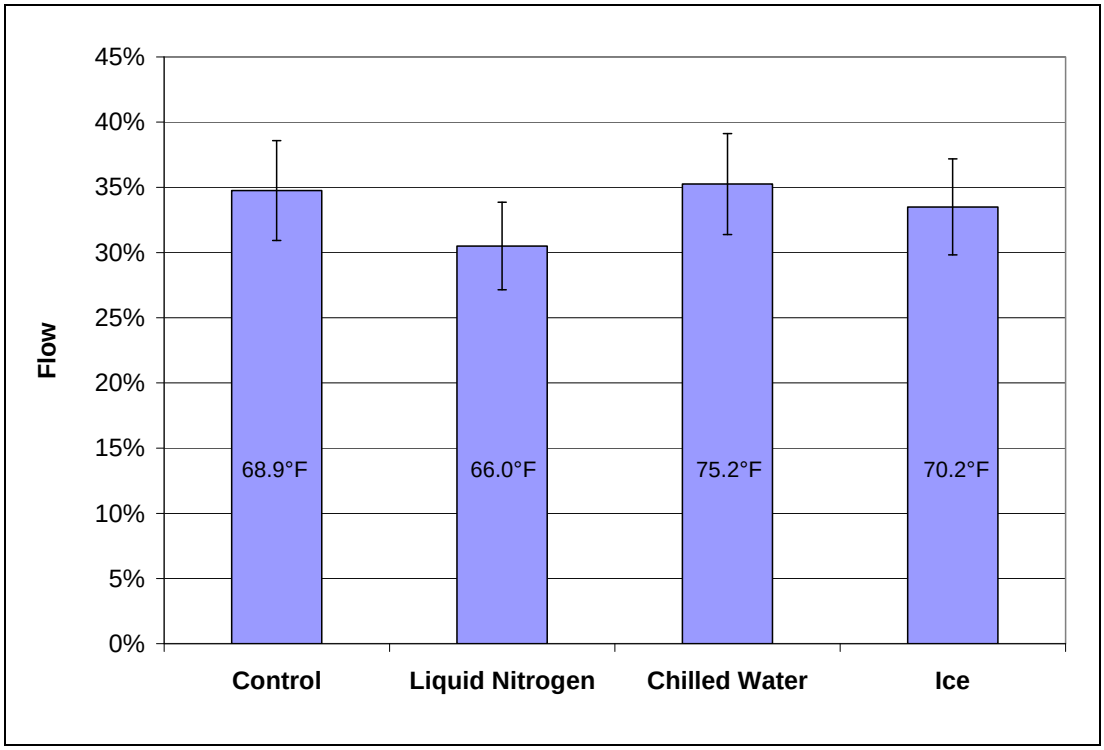


FIGURE 3.3 Flow of cement mortar containing ADVA Flow

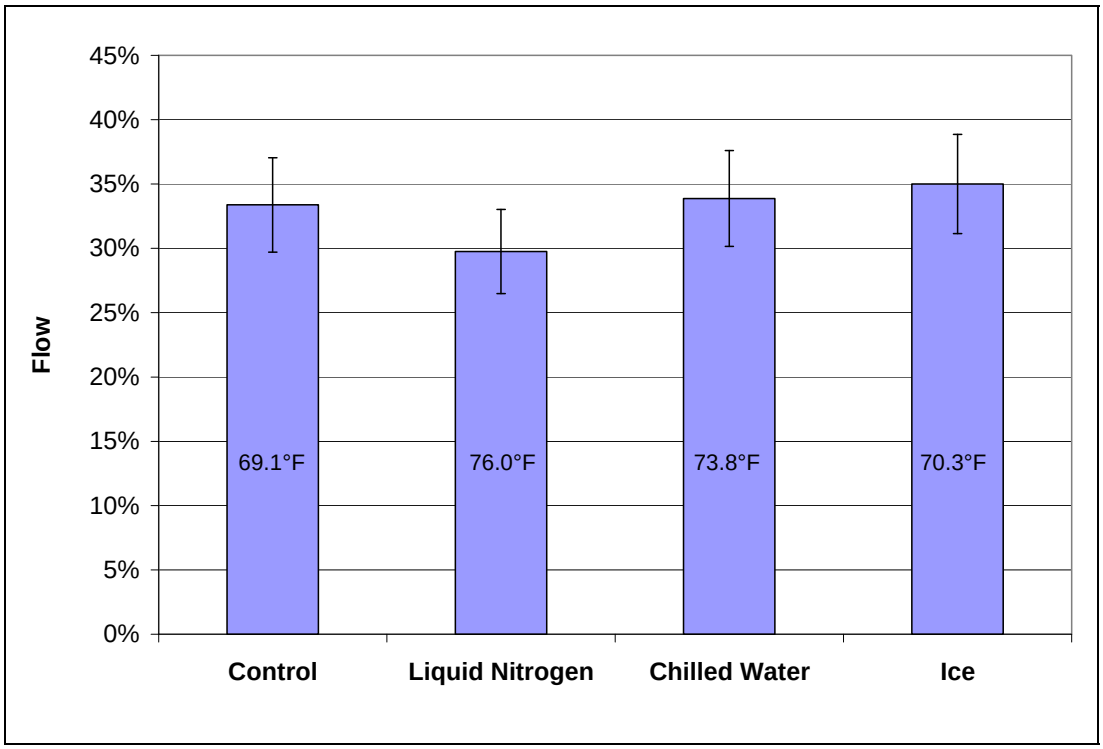


FIGURE 3.4 Flow of cement mortar containing Pozzolith 961R

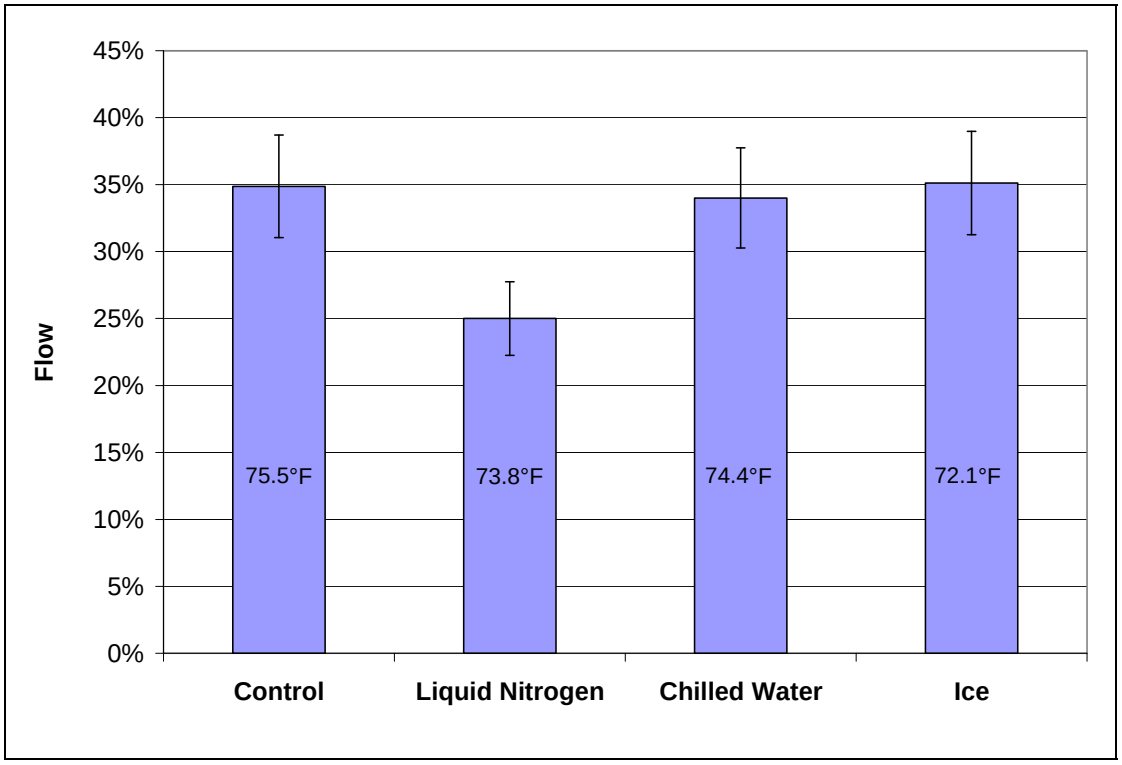


FIGURE 3.5 Flow of cement mortar containing Pozzolith 200N

3.2.3 Discussion of Flow Testing

Results from flow testing indicate that LN had little effect on the flow of cement mortar, except in the case of cement mortars containing Pozzolith 200N, as shown in Figure 3.5. The flow measurement of the LN specimen in this case is somewhat lower than the control, chilled water, and ice specimens. Repeated testing of the LN cooled specimen also showed that the flow was lower in comparison with the control, chilled water, and ice mixtures, independent of mortar temperature. The flow of mortars containing Pozzolith 200N cooled with LN to 68.5°F and 66.1°F were 25.50% and 26.63%, respectively.

3.3 FRESH PROPERTIES OF CONCRETE

One of the biggest concerns with using LN is the effect that it will have on the fresh properties of concrete. Maintaining consistency in fresh concrete properties is

already very difficult without the addition of LN. Therefore, it is important to determine how LN changes concrete slump and setting time. Furthermore, if fresh concrete properties are affected, it is vital to determine if the results are reversible or how to reverse the effects so concrete placement and curing are not impacted. This section deals specifically with the effects of LN on the fresh concrete properties of slump, setting time, and yield.

3.3.1 Concrete Mixing Materials

Concrete mixing materials were procured through a variety of sources. The materials are representative of those used by Transit Mix Concrete and Materials Company in Austin, Texas for TxDOT mass concrete applications. A list of the materials, material types, and suppliers is shown in Table 3.2. In addition, a cement oxide analysis is shown for the TXI Type I/II cement in Table 3.3 and aggregate gradations and properties are shown in Table 3.4.

TABLE 3.2 Material Suppliers and Selections for Full-Scale Concrete Mixtures

Materials	Type	Supplier
Cement	I/II	TXI
Coarse Aggregate	3/4" limestone river gravel	Capitol Aggregate
Fine Aggregate	Natural Sand	Capitol Aggregate
Low Range Water Reducer	WRDA 35	W.R. Grace
Water Reducer/Retarder	Daratard 17	W.R. Grace
Midrange Water Reducer	Daracem 65	W.R. Grace
Polycarboxylate Superplasticizer	Advaflow	W.R. Grace
Naphthalene Superplasticizer	Daracem 19	W.R. Grace
Vinsol Resin	Daravair 1000	W.R. Grace
Synthetic Air Entrainer	Darex AEA	W.R. Grace
Fly Ash	F	Boral (Bowen)
Fly Ash	C	Boral (Deely)
Slag	120 Grade	Holnam
Silica Fume	Force 10,000D	W.R. Grace

TABLE 3.3 Oxide Analysis for Type I/II Cement used in Concrete Mixtures

Name	Chemical Formula	Weight (%)
Silicon Dioxide	SiO_2	20.12
Aluminum Oxide	Al_2O_3	4.74
Iron Oxide	Fe_2O_3	2.98
Calcium Oxide	CaO	64.21
Magnesium Oxide	MgO	1.43
Sodium Oxide	Na_2O	0.21
Potassium Oxide	K_2O	0.46
Titanium Dioxide	TiO_2	0.18
Manganic Oxide	Mn_2O_3	0.34
Phosphorous Pentoxide	P_2O_5	0.05
Strontium Oxide	SrO	0.04
Barium Oxide	BaO	0.03
Sulfur Trioxide	SO_3	2.50
Loss on Ignition		2.70

Tricalcium Silicate	C_3S	65.24
Tricalcium Aluminate	C_3A	7.52
Dicalcium Silicate	C_2S	8.48
Tetracalcium Aluminoferrite	C_4AF	9.07

TABLE 3.4 Gradations and Properties for Aggregate used in Concrete Mixtures

Coarse Aggregate Gradations (3/4" Blend)		
Sieve Sizes	ASTM C33 Gradation	Percent passing
1 in.	100	100
3/4 in.	90 - 100	90
3/8 in.	20 - 55	35
No. 4	0 - 10	6
No. 8	0 - 5	1
Fine Aggregate Gradations (Concrete Sand)		
Sieve Sizes	ASTM C33 Gradation	Percent passing
3/8 in.	100	100
No. 4	95 - 100	98
No. 8	80 - 100	88
No. 16	50 - 85	70
No. 30	25 - 60	49
No. 50	5 - 30	20
No. 100	0 - 10	5
No. 200	0 - 5	1
Fineness Modulus	2.3 - 3.1	2.7
Aggregate Properties		
	Coarse Aggregate	Fine Aggregate
Oven Dry Unit Weight (lb/ft^3)	104.2	112.2
OD Specific Gravity (%)	2.58	2.61
Absorption (%)	1.58	0.77

3.3.2 Concrete Experimental Matrix and Mixture Design

The concrete testing matrix in Table 3.5 was developed to incorporate supplementary cementing materials (SCMs) and chemical admixtures that may be found in hot weather concreting and mass concrete applications. In addition, combinations of SCMs and chemical admixtures were tested to determine if LN would affect them

differently when combined. The SCMs used in the concrete mixtures consisted of ASTM C 618-05, “Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete,” Class C and Class F ashes and a ground granulated blast furnace slag..

The concrete mixture design shown in Table 3.6 represents typical proportions for a one cubic yard concrete mixture. When SCMs were used, a certain percentage of cement was replaced with the same percentage of SCM, thereby maintaining the cementitious content and water-to-cementitious materials ratio. The second column in Table 3.6 shows the actual proportions that were needed to fabricate all testing specimens. Each concrete mixture was used to make 27 - 4”x 8” cylinders, 2 – 6”x12” cylinders, and one Chinese take-out box (for hardened air void testing) with the following dimensions: 4.75 in. long, 3.75 in. wide and 4.00 in. high. Results from tests were compared between batches where all materials were at room temperature (~73°F) to those where ingredients were stored at 100°F and cooled to room temperature using LN.

TABLE 3.5 Testing Matrix for Full-Scale Concrete Mixtures

Mix Number	Mix Description	Chemical Admixture (fl.oz per 100 lbs cementitious materials)	SCM Type (% replacement)
01	Control	x	x
02	F Ash	x	Bowen (50%)
03	Low Range Water Reducer	WRDA 35 (6.0)	x
04	Water Reducer/Retarder	Daratard 17 (3.0)	x
05	Midrange Water Reducer	Daracem 65 (9.0)	x
06	Polycarboxylate Superplasticizer	ADVA Flow (7.3)	x
07	Naphthalene Superplasticizer	Daracem 19 (16.0)	x
08	Air + Water Reducer	Daravair 1000 (0.35) + ADVA Flow (6.0)	x
09	Slag + Water Reducer	ADVA Flow (5.0)	Slag (50%)
10	F Ash + Water Reducer	ADVA Flow (4.0)	Bowen (30%)
11	Silica Fume + Water Reducer	ADVA Flow (6.0)	Silica Fume (8%)
12	Slag	x	Slag (50%)
13	C Ash + Water Reducer	ADVA Flow (3.0)	Deely (30%)
14	C Ash	x	Deely (30%)
15	F Ash	x	Bowen (30%)
16	Air + Water Reducer	Darex AEA (0.15) + ADVA Flow (4.0)	x
17	Silica Fume + Water Reducer + Air	Darex AEA (0.20) + ADVA Flow (7.0)	Silica Fume (8%)
18	F Ash + Water Reducer + Air	Darex AEA (0.35) + ADVA Flow (4.0)	Bowen (30%)
19	C Ash + Water Reducer + Air	Darex AEA (0.15) + ADVA Flow (4.0)	Deely (30%)
20	Slag + Water Reducer + Air	Darex AEA (0.25) + ADVA Flow (6.0)	Slag (50%)

TABLE 3.6 Concrete Mixture Design (for plain concrete, w/c=0.44)

Material	lb/yd^3	lb/3.16 ft^3
Cement	564	66.1
Water	248	29.1
Coarse Aggregate	1,800	211
Fine Aggregate	1,450	170

3.3.3 Concrete Mixing Procedure

After charging the mixer with materials, the concrete was mixed for 3 minutes, allowed to rest for 2 minutes, and then mixed again for 3 more minutes. Normal room temperature mixtures continued mixing through the last 3 minutes with no disturbance. For the cooled mixtures, LN was injected during the last 3 minutes of mixing until the concrete mixture temperature was lowered to 73°F.

In the early tests (mixtures 1-15), the mouth of the concrete mixer was left uncovered during mixing, allowing water vapor to flow freely from the mixing drum, as shown in Figure 3.6. Typically, the water vapor filled the entire mixing room with a cool, dense fog. Some concerns were raised with regard to water evaporating from the concrete during mixing due to LN. LN is so cold and so dry that it either freezes water or condenses moisture from the air. In the case of concrete, LN removes moisture from the concrete because it reduces the local relative humidity and increases evaporation from the mixture. This situation lowers the water-to-cement ratio of the mixture, potentially causing false reductions in slump and artificial increases in compressive strength. A modified mixing experiment was performed to verify that water was indeed being lost from the mixer during LN injection.

A preliminary test for water vapor involved the use of a hygrometer, which measures relative humidity. Since the mixing room was temperature-controlled at 73°F ± 2°F, the humidity in the room did not fluctuate very much. Therefore, any increase in relative humidity during LN dosing of a concrete mixture would indicate that water was evaporating from the mixing drum. Results from two hygrometer tests indicated that

water vapor from the concrete mixtures was indeed causing the relative humidity in the mixing room to increase. The relative humidity increased from 65% to 74% during the first test and from 60% to 66% in the second test.

One additional water loss test was performed to minimize vapor emission during LN injection. During the entire mixing process, a hard, plastic cover was placed over the mouth of the concrete mixer, as shown in Figure 3.7, and will be discussed in section 3.3.4.1. A small flap that could be opened and closed was cut into the center of the cover to enable LN dosing. Although, the cover was not completely air-tight, the tests demonstrated the reduction in water loss was considerable and helped to eliminate another variable in the testing results. Therefore, the later mixtures (16-20) were conducted with the mixer covered.

FIGURE 3.6 Liquid nitrogen vapor flows freely from the uncovered mixer

FIGURE 3.7 Plastic cover with hole in the middle for liquid nitrogen dosing

3.3.4 Concrete Slump

The slump test is performed to ensure that a concrete mixture is workable. The measured slump must be within a specified range, or tolerance, from the target slump. One of the biggest drawbacks to hot weather concreting is the significant loss of slump due to rapid hydration caused by the heat. The use of LN should lower the concrete temperature and decrease the rate of cement hydration to reduce slump loss. However, it was hypothesized that the application of LN may cause localized freezing of the concrete which could result in decreased slumps.

Slump tests are performed according to ASTM C 143, "Standard Test Method for Slump of Hydraulic Cement Concrete" (ASTM C 143, 2003). Concrete is placed in 3 separate layers into a metal cone, as shown in Figure 3.8. The concrete is then compacted by inserting a metal rod in and out of the concrete 25 times. This procedure is repeated for all 3 layers. Once all the concrete is compacted, the top surface is leveled

off and the cone is lifted straight up, away from the concrete. The rod is then placed on top of the slump cone and the difference between the bottom of the rod and the top of the concrete is measured. Slump is measured in inches and can be anywhere from 0 to 10 inches. Low slump concrete is stiff and very difficult to place and finish. High slump concrete is rather fluid and easily placed. A typical slump value for most applications ranges from 3 to 5 inches. However, for slip-form construction, a maximum slump of 2 inches is required. For heavily congested pours, a slump of 7 inches may be required. Therefore, the target slump is determined based on concrete use.

FIGURE 3.8 Slump cone and rod used in slump testing

3.3.4.1 Results of Slump Testing for Laboratory Mixed Concrete

The slump results in Figures 3.9 show a comparison between the control mixtures (73°F) and the LN mixtures that were cooled to 73°F from 100°F. The mixture numbers in the figure correspond to the mixture numbers shown in Table 3.5. The mixture numbers in this table will be referenced often when discussing the results of the different concrete tests. The research presented in this section compares slump results between concrete batches where all materials were at 73°F to those where ingredients were stored at 100°F and cooled to 73°F using LN.

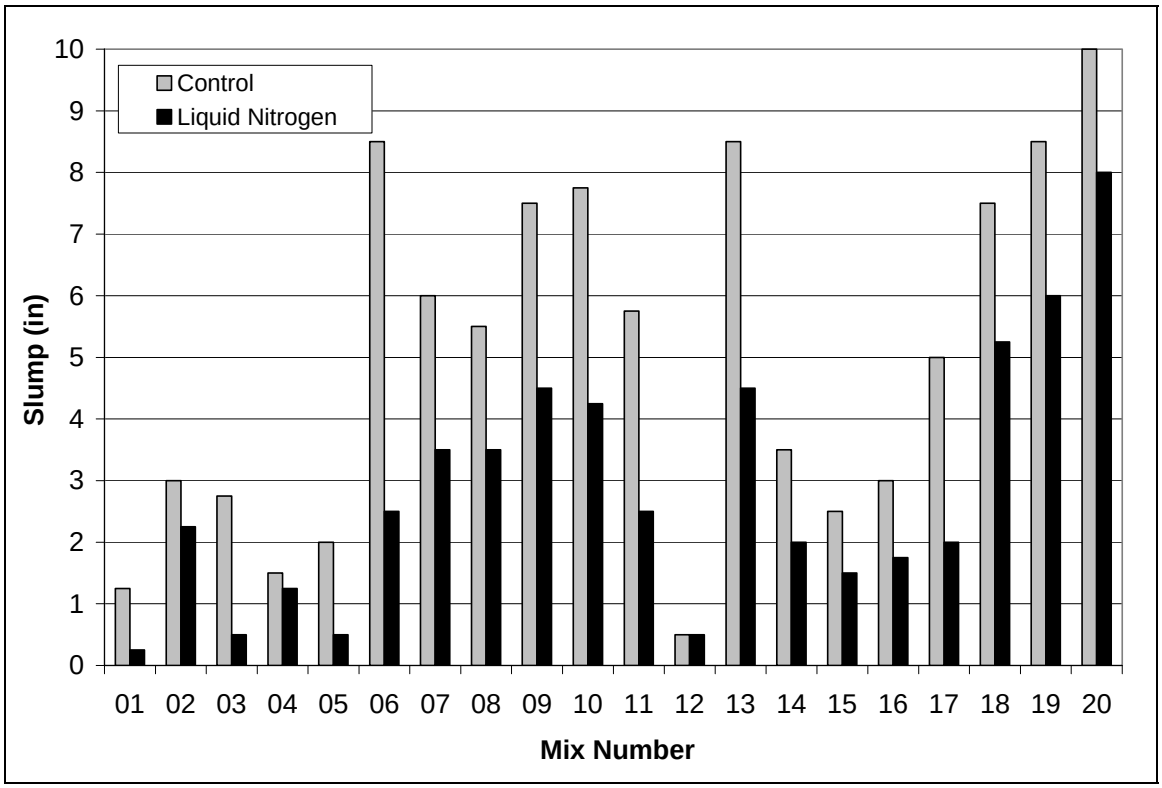


FIGURE 3.9 Slump results for room temperature and liquid nitrogen cooled concrete

Data presented in Figure 3.9 show that the slump for LN cooled concrete is lower in all cases than the control mixtures. For some mixtures, the difference between the control and the LN mixtures is quite dramatic. For example, the slump for the LN mixture is 6.0 inches less than the control for mixture 6, 3.5 inches less for mixture 10,

and 4.0 inches less for mixture 14. ASTM C 143 states that the acceptable difference between two separate slump test results is 0.65 inches for a slump between 1 and 2 inches, 1.07 inches for a slump between 3 and 4 inches, and 1.13 inches for a slump 6.5 inches and greater. Based on these criteria, mixtures 02 (F ash), 04 (water reducer/retarder), and 12 (slag) are the only mixtures that do not show significant differences between the room temperature control and the LNCC. The difference in the slump for all the other mixtures is significant, indicating that LN does reduce the slump of fresh concrete.

As stated earlier, there is concern that LN removes moisture from concrete. This could potentially result in a decrease in the water-to-cement ratio and a subsequent decrease in slump. Therefore, testing was performed to determine if water was evaporating from concrete mixtures. During LN dosing, a hard, plastic cover was placed over the entire mouth of the concrete mixer to minimize vapor emission, thereby maintaining the water content in the concrete mixture. However, the plastic cover did not form a complete seal over the mixing drum, and some water vapor escaped.

Testing was conducted on two separate concrete mixtures, mixtures 6 and 10. Mixture 6 contained 564 lbs. (6 sacks) of Type I/II cement with a polycarboxylate superplasticizer. Mixture 10 was a Type I/II cement mixture, 30% F ash replacement (Bowen) with a polycarboxylate superplasticizer. The plastic cover mixing procedure was varied to compare the slumps of “covered” mixtures against “uncovered” mixtures. It was expected, therefore, that the slump of the covered concrete mixtures (some water loss) should fall between the room temperature control mixture (no water loss) and the uncovered concrete mixture (more water loss).

Results of slump testing on covered and uncovered concrete confirm that water evaporation is contributing to slump loss, as shown in Figure 3.10. As expected, the control mixture had the highest slump. The uncovered mixture had the lowest slump since it had the greatest amount of water loss. The slump of the covered mixture was between the control and the uncovered mixture since water evaporation was reduced. Therefore, minimizing vapor loss will maintain the expected slump of a concrete mixture.

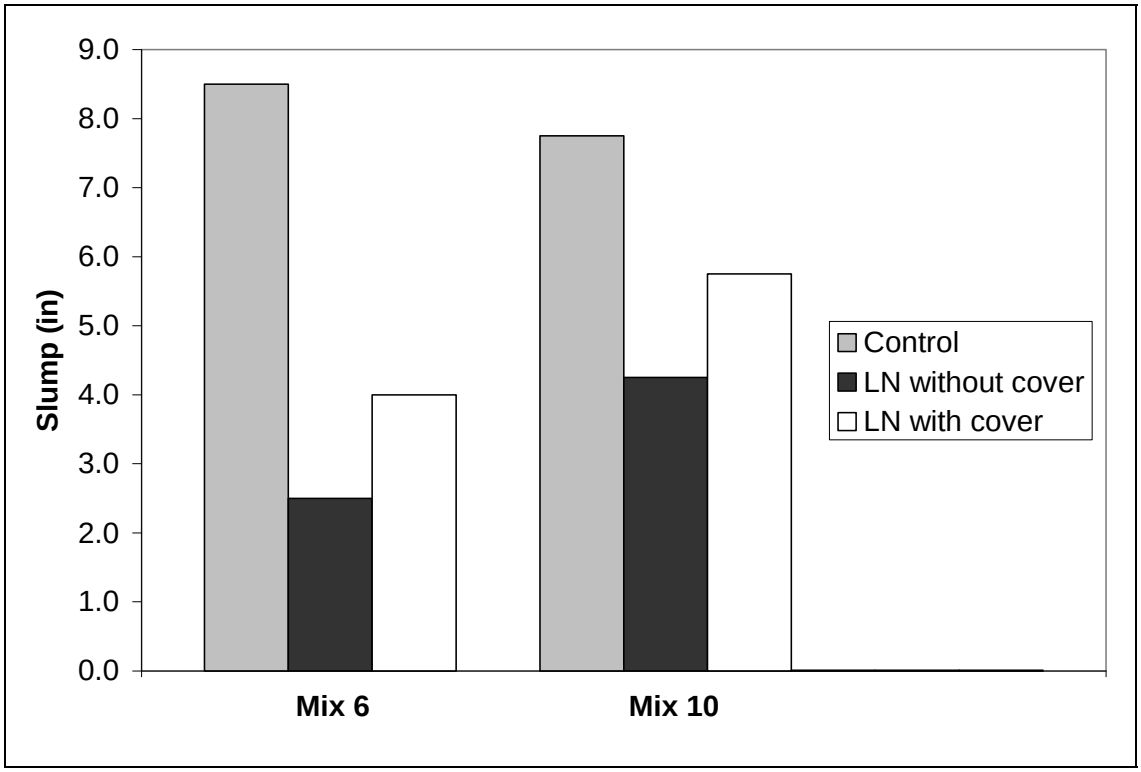


FIGURE 3.10 Slump comparison of room temperature, covered, and uncovered concrete

A comparison of slump data for mixtures 1-15 (uncovered) and mixtures 16-20 (covered) shows that covering the concrete mixer to reduce vapor emission did actually not have a significant effect on reducing slump loss of LNCC. The results, however, indicate that an unaccounted variable was causing a reduction in slump. Further testing was conducted on field-mixed concrete to determine if slump loss was specific to laboratory mixed concrete.

3.3.4.2 Results of Slump Testing for Field Mixed Concrete

Slump testing on field-mixed concrete was performed to confirm the results of laboratory testing. Field mixed concrete was sampled from concrete trucks at the Transit Mix batch plant in Round Rock, Texas. Sampling occurred in August 2006 on concrete that was to be used as rip rap to stabilize the sides of an open channel waterway. The ambient temperature was approximately 105°F, which necessitated the use of LN for

mass concrete, bridge decks, and pavements to ensure that they met temperature specifications. Rip rap concrete does not a have a temperature specification and it was not necessary to dose the concrete. However, Transit Mix dosed the rip rap concrete anyway to assist in the research. Concrete was discharged into a wheelbarrow before LN dosing and again after LN dosing was complete. This is different than the testing that was conducted in the laboratory. In the lab, slump testing was always conducted on concrete that was at 73°F. Control mixtures were stored and mixed at 73°F and LN mixtures were preheated to 100°F and then cooled to 73°F before slump testing. With the field testing, it was impossible to keep the control mixtures at 73°F since the materials were stored outside in the hot sun. Therefore, slump testing was conducted on hot concrete mixtures before LN dosing occurred and then on the same mixture after LN dosing had occurred. The comparison of these results do not correlate directly to laboratory mixed concrete, but these results are the best available from the field. Slump results for field testing are shown in Figure 3.11.

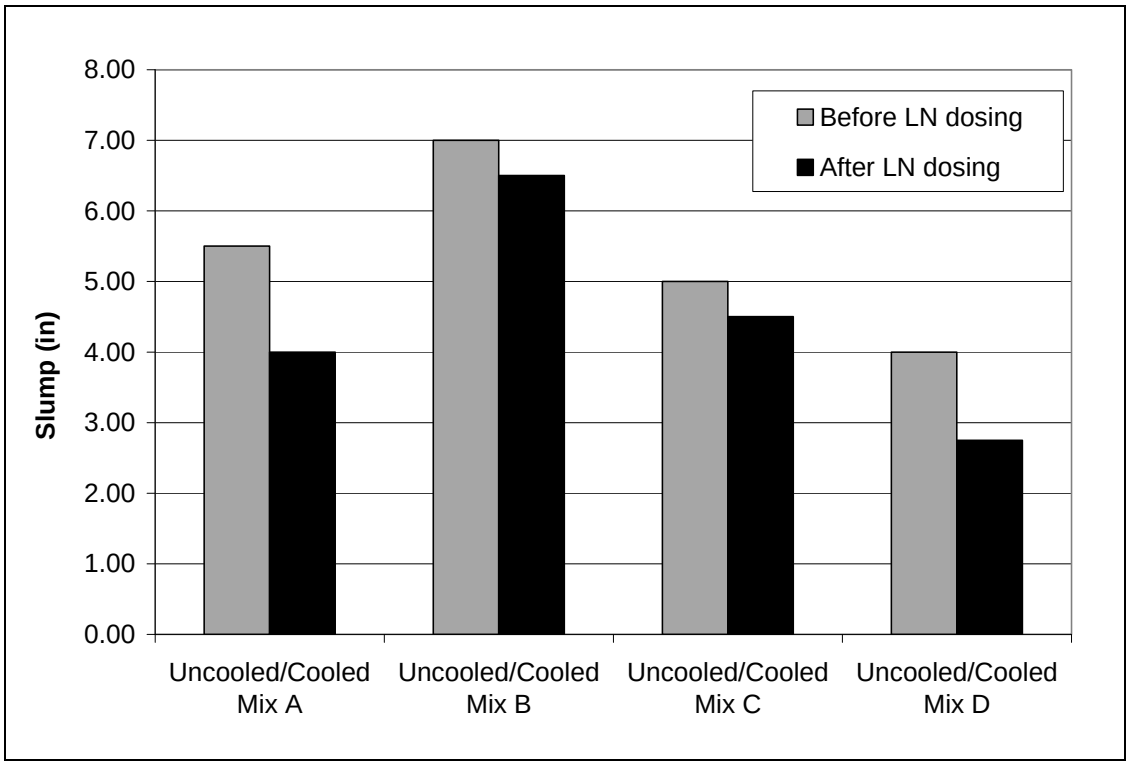


FIGURE 3.11 Slump results for field mixed concrete

The data show that slump is lower for all field mixtures after LN dosing. ASTM C 143's criteria indicate, though, that only field mixtures A and D show significant differences between the original and the cooled concrete. There are three factors that affect slump in this study, independent of LN. First, slump always decreases with time due to the progress of the hydration reactions, a phenomenon called slump retention or slump loss. Second, slump is always lower at higher temperatures. Third, rip rap concrete is generally a lean mixture and may affect slump response to LN. Considering the first factor, it would be expected that the LN-cooled samples would have a lower slump than the pre-cooled samples because of sampling time. Considering the second factor, it would be expected that the pre-LN samples would have a lower slump because of their higher temperature. Since the data show that LN cooled samples generally have lower slumps, it's likely that the fresh temperature effect is small or contrary to expectation. The time effect may have influenced these results, and this may be in combination with an effect of LN. Considering the third factor, slump results may be affected by the relatively small amount of cement in the mixture, which may minimize the effects of LN. To separate these effects, further laboratory testing was conducted to examine the effects of temperature, time, and LN on slump.

3.3.4.3 Slump Retention Results for Laboratory Mixed Concrete

Slump retention testing was performed in the laboratory to determine to cause of the reduction of slump due to LN dosing and to investigate the effects of time. Furthermore, the testing investigated the effects of temperature on slump to determine the rates at which hot and cold concretes lose slump. In previous concrete testing, laboratory slump measurements were taken only on 73°F concrete mixtures while field mixtures compared slump measurements from 73°F concrete and 100°F concrete. Slump retention testing incorporated 73°F, 100°F, and 40°F concrete mixtures and varied the time at which dosing occurred. The control mixture (A) was made with materials mixed at 73°F and tested at 73°F. Mixture B was made with materials heated to 100°F and tested at 100°F to see the effect of temperature. Mixtures C - F were made with materials heated to 100°F and cooled to 73°F with LN at 0, 15, 45, and 60 minutes, respectively. Mixtures

G and H were made with materials heated to 100°F and cooled to 40°F with LN at 0 and 60 minutes, respectively, again to see the effects of temperature. Slump retention data for mixtures A - H are shown in Figure 3.12.

The slump measurements in the graph are plotted against the time from the start of mixing. In other words, the 8 minute data point was a slump measurement taken 8 minutes after water was poured into the concrete mixtures. This time marker was selected since proper mixing and cooling of the concrete mixtures required 8 minutes. Slump tests were performed immediately following cooling. For mixtures that were not cooled immediately (mixtures D-F and H), slump measurements were performed on 100°F concrete until the mixtures were cooled at the specified time. For example, the slump measurements taken at 8, 15, 30, and 45 minutes for mixture F were on 100°F concrete. The slump measurements at 60, 75, 90, 105, and 120 minutes were taken on 73°F concrete.

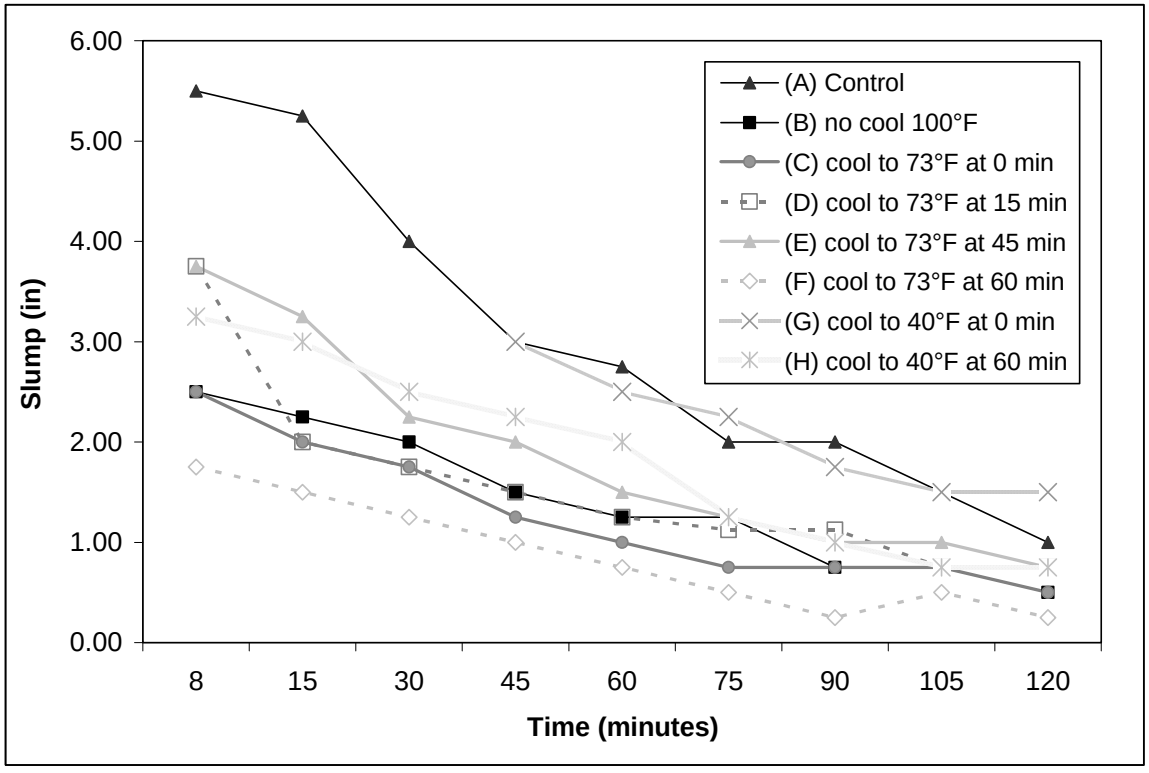


FIGURE 3.12 Slump retention for concrete mixtures cooled with liquid nitrogen to varying temperatures and at varying time

The data in Figure 3.12 indicate that slump is strongly influenced by the initial temperature of the mixture, regardless of whether or not cooling was used. The control mixture A, the only mixture that never had ingredients stored at 100°F, had a much higher slump that the rest of the mixtures. That the 73°F control sample has a higher slump than the LN-cooled mixtures is consistent with the results shown in Figure 3.9. All the mixtures cooled from 100°F to 73°F have similar initial slump and slump retention to the mixture that was always at 100°F. In this testing, LN cooling did not reduce the initial slump more than that of the 100°F mixture. This is slightly different than the comparable field data in Figure 3.11 which showed slightly lower slumps for the LN-cooled mixtures. Since slump loss is rapid with time, it is likely that the differences in slump in Figure 3.11 are due to the time of testing.

These results suggest that the lower slump experienced in LN cooled concrete is actually caused by preheating of the mixing materials and not by LN. The immediate hydration reactions that occur when cement and water are combined are rapidly accelerated by the heat, thereby causing a significant decrease in slump right away, which is not reversible upon cooling.

With respect to the rate of slump retention, it appears that the rate remains relatively constant for all mixtures except for the control mixture. The control mixture loses slump at a more rapid rate than the preheated mixtures so that at the end of two hours, the slump of the control mixture is virtually the same as the preheated mixtures.

The results of cooling to 40°F are interesting. It would be expected that concrete at 40°F should have a higher slump than the control mixture A. This is not the case, likely due to the preheating effect. However, when cooled to 40°F very quickly, mixture G, the slump curve closely matches that of the 73°F curve, and is higher than the 100°F curve. Unfortunately, early data points are missing from mixture G because it required approximately 30 minutes of LN dosing to lower the temperature from 100°F to 40°F. Therefore we cannot tell if the initial slump for mixture G was higher due to the early cooling to a much lower temperature. In the case of mixture H, there are no missing data points since adjustments were made to the flow of LN so that the mixture was cooled within 10 minutes of dosing. These data are similar to the 100°F mixture, indicating that the effects of extended pre-heating cannot be reversed by “super-cooling.”

3.3.4.4 Conclusions for Slump Tests

Figures 3.9 and 3.11 show a decrease in slump for concrete cooled with LN. Figure 3.10 suggests that slump loss results from water evaporation during LN dosing. However, the results of further testing shown in Figure 3.12 data show that slump loss was not, in fact, caused by LN dosing but by preheating of the mixing materials. All mixtures cooled with LN had initial slump and slump retentions similar to a 100°F mixture, while a 73°F mixture had a much higher slump. This is a promising result for users of LN because it demonstrates that this technique is not reducing slump. In fact, practitioners would not notice any slump loss with LN because the direct comparison will always be with a hotter, un-cooled control mixture. The downside is that LN cannot be used as a countermeasure against temperature-related slump loss.

3.3.5 Setting Time

Setting of concrete is the gradual conversion from a plastic, moldable material to a solid capable of resisting considerable loads. The point at which concrete is considered to have set is somewhat arbitrary. ASTM C 403, "Standard Test Method for Time of Setting of Concrete Mixtures by Penetration Resistance," divides setting of concrete into initial and final set (ASTM C 403, 1999). Initial and final set times are important because they give an indication of when the concrete can be properly placed, consolidated and finished. Time of set tests are performed on mortar samples that are obtained by wet-sieving fresh concrete and measuring the force required to penetrate needles of various diameters into the mortars. A photograph of a penetrometer is shown in Figure 3.13. Initial and final set are defined as a penetration resistance of 500 psi and 4000 psi, respectively. Typically, a concrete contractor considers initial set as the time at which a concrete surface can bear the weight of person with minimal indentation and final set as the point where finishing is no longer possible.

The curing temperature of concrete is an important factor governing setting time. Higher curing temperatures result in faster reactions between cement and water, causing rapid setting in concrete. Increased rates of setting result in greater difficulty in placement, consolidation, and finishing. Slowing the rate of setting in hot weather can be

achieved by lowering the concrete temperature, either through the use of SCMs or possibly LN. The use of LN to cool concrete may prolong setting to ensure proper placement and finishing of concrete. Decreased concrete temperatures slow cement hydration reactions and increase setting times. However, localized freezing within a concrete mixture may extend setting times excessively, leaving the concrete at greater risk for plastic shrinkage and possibly delaying construction projects. The focus of this section is to determine the effect of LN on the setting time of fresh concrete.

FIGURE 3.13 Initial and final set of fresh concrete are measured with a penetrometer

3.3.5.1 Results of Setting Time Tests on Laboratory Mixed Concrete

The initial and final set time data in Figures 3.14 and 3.15 show a comparison between the control mixtures (73°F) and the LN mixtures that were cooled to 73°F from

100°F. Further details as to the composition of each mixture are in Table 3.5. The bars in the setting time graphs show the overall time needed for each mixture to reach final set. The gray portion of the bar shows the time required for each mixture to reach initial set. The black portion of the bar indicates the additional time required to go from initial set to final set.

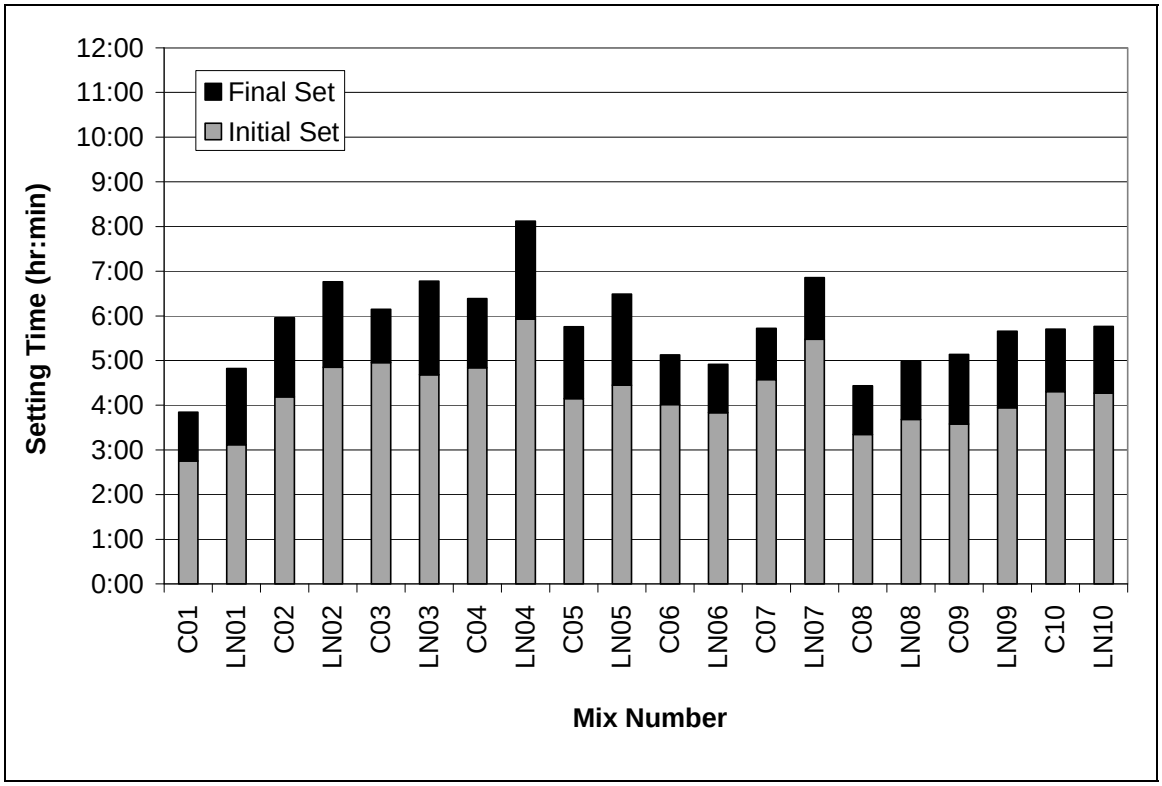


FIGURE 3.14 Initial and final set times for concrete mixtures 1-10

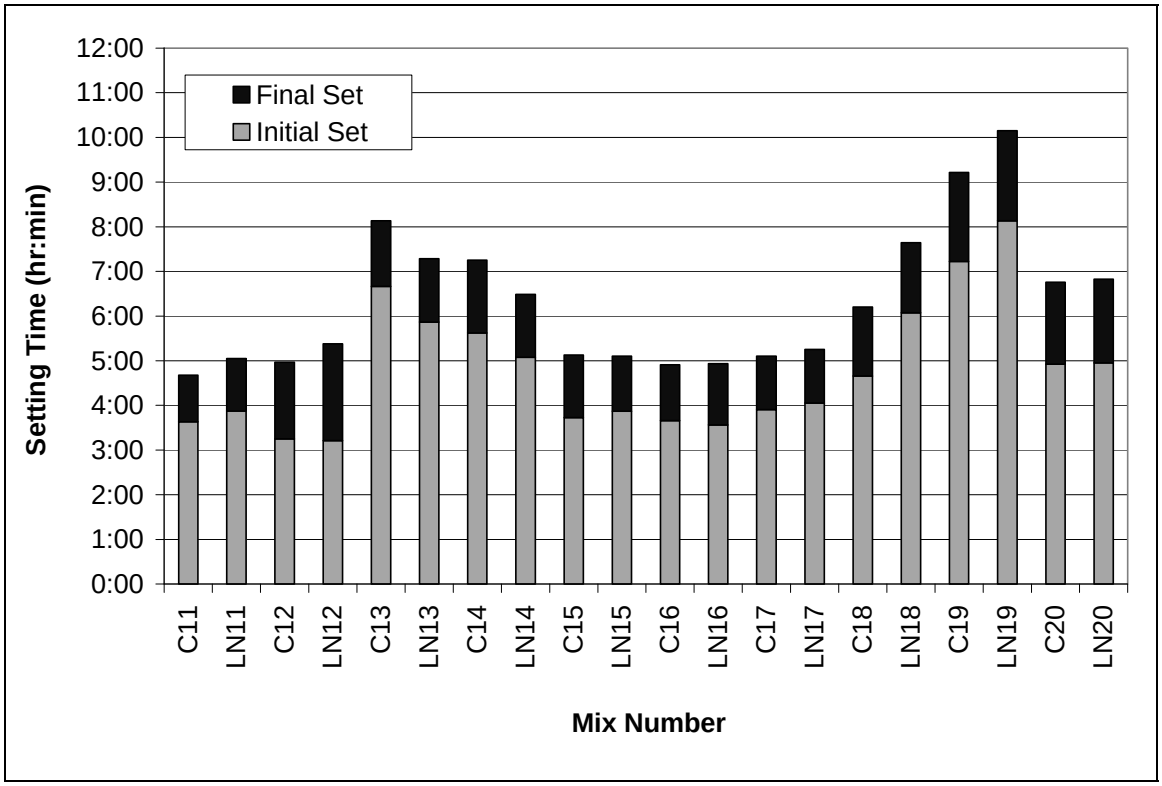


FIGURE 3.15 Initial and final set times for concrete mixtures 11-20

Data presented in Figures 3.14 and 3.15 show that the time required to reach final set for LN-cooled concrete is longer in all but 4 mixtures. In mixtures 06 (polycarboxylate superplasticizer), 13 (C ash/water reducer), 14 (C ash), and 15 (F ash), the time to reach final set was lower for LN cooled mixtures than it was for the control mixtures. To determine if the difference in set times was significant, the precision statement in ASTM C 403 was used; this states that the single operator range of results should not exceed 23% for initial set and 16% for final set. Table 3.7 shows the percent difference for the setting time between control and LN mixtures. A positive percentage indicates that the LN mixture took longer to set than the control mixture, while a negative percentage indicates that the LN mixture set faster than the control mixture. Numbers in bold denote that the mixture has exceeded the precision threshold in ASTM C 403.

Mixtures 01 (control), 04 (water reducer/retarder), and 07 (naphthalene superplasticizer) are the only mixtures in which the difference in setting time between the

control and LNCC are significant, and only for final set. For these mixtures, the time to reach final set was longer than the 16% threshold between the control and the LN mixtures. Mixtures 01, 04, and 07, however, only represent 15% of the entire mixing matrix. Therefore, it appears that the use of LN to cool concrete does not have a significant effect on the final setting time of concrete for these samples. In comparing the setting times for uncovered (1-15) and covered (16-20) concrete mixtures, the covered concrete mixtures behaved similarly to the uncovered mixtures. Table 3.7 shows insignificant differences in the time to reach initial and final set except for mixtures 01, 04, and 07. These particular mixtures, however, only represent 15% of the entire mixing matrix. It appears from the data that uncovered versus covered mixtures has no effect on setting time.

The window of finishability is the time between initial and final set where concrete craftsmen finish and texture the concrete surface. Extending the window of finishability would leave the concrete susceptible to plastic shrinkage and may extend the project. Shortening that window would require finishers to work faster and would potentially force them to sacrifice quality for the sake of time. The data in Figures 3.14 and 3.15 show that the window of finishability when comparing control and LNCC of the same mixture is approximately the same. Table 3.7 shows the percent increase in the window of finishability between the control and LN mixtures. A positive percentage indicates a greater window of finishability for LN mixtures than for the control mixtures. A negative percentage indicates a smaller window of finishability. Most of the mixtures (80%) showed an increase in the window of finishability with LN cooling. Mixtures 01 (control), 03 (low range water reducer), and 04 (water reducer/retarder) had the most dramatic increase of 57%, 76%, and 42%, respectively in the window of finishability. The remainder of the mixtures experienced a less than 30% increase in the window of finishability, with 15 out of the 20 mixtures staying below 20%. Since the change in the window of finishability is so small for so many of the mixtures, it can be concluded that LN does not significantly affect the time between initial and final set.

It should be noted that these tests were done under laboratory conditions. The specimens of sieved mortar were stored at 73°F in all cases. Given that the specimen sizes are small relative to the sizes of actual concrete members in the field, the

temperatures of the specimens reached equilibrium (73°F) rather quickly, even for the hotter specimens. Therefore, these laboratory conditions do not mimic field conditions well. In the field, the ambient temperature will be hotter than 73°F and the concrete will be surrounded, and therefore insulated, by concrete of the same temperature. Sonia Solt (Solt, 2006) performed both laboratory and field experiments examining the effects of temperature and LN cooling on setting. In her laboratory studies, samples were kept insulated and in varied ambient environments to mimic field conditions. She observed that LN consistently extended setting time, an effect that was not observed in the work reported here because of artifacts introduced by the laboratory environment.

TABLE 3.7 Difference in Setting Times for Control and Liquid Nitrogen Mixtures

Mix	**Initial Set (23% max)**	**Final Set (16% max)**	**Window of Finishability**
	% difference between control and LN mixes		
1	13.2%	**25.6%**	57%
2	15.8%	13.6%	8%
3	-5.6%	10.2%	76%
4	22.5%	**27.2%**	42%
5	7.2%	12.6%	27%
6	-4.4%	-4.1%	-3%
7	19.7%	**19.9%**	20%
8	10.2%	12.2%	18%
9	10.1%	10.1%	10%
10	-0.9%	1.1%	7%
11	6.6%	8.0%	13%
12	-1.2%	8.3%	26%
13	-12.0%	-10.5%	-4%
14	-9.8%	-10.6%	-13%
15	3.8%	-0.4%	-12%
16	-2.6%	0.5%	10%
17	3.8%	2.9%	0%
18	3.5%	0.1%	1%
19	3.2%	4.0%	1%
20	0.6%	1.0%	2%

3.3.5.2 Effects of Temperature on Setting Time

In normal concrete mixtures, temperature determines the rate at which concrete sets. Colder temperatures slow the rate of hydration, subsequently delaying the time of set. Hotter temperatures accelerate the hydration reactions and cause the concrete to set faster. Experiments were performed to investigate how the window of finishability would be affected and if the setting times are affected by concrete that is cooled far below TxDOT's minimum concrete specification temperature. The concrete mixtures for this experiment used Type I/II cement, 30% Class F fly ash, 0.44 water-cement ratio, and a midrange water reducing admixture. Figure 3.16 shows setting time data for 4 concrete mixtures with varying temperatures to which they were cooled:

A. Control: All mixing materials were stored at 73°F and mixed at 73°F.
B. All mixing materials were stored and mixed at 100°F.
C. All mixing materials were stored and mixed at 100°F and cooled to 73°F with liquid nitrogen.
D. All mixing materials were stored and mixed at 100°F and cooled to 40°F with liquid nitrogen.

After the concrete mixtures were finished mixing, they were all kept in a 73°F temperature controlled room during setting time testing. Each mixture eventually came into equilibrium with the room environment so that even the 100°F mixture cooled to 73°F.

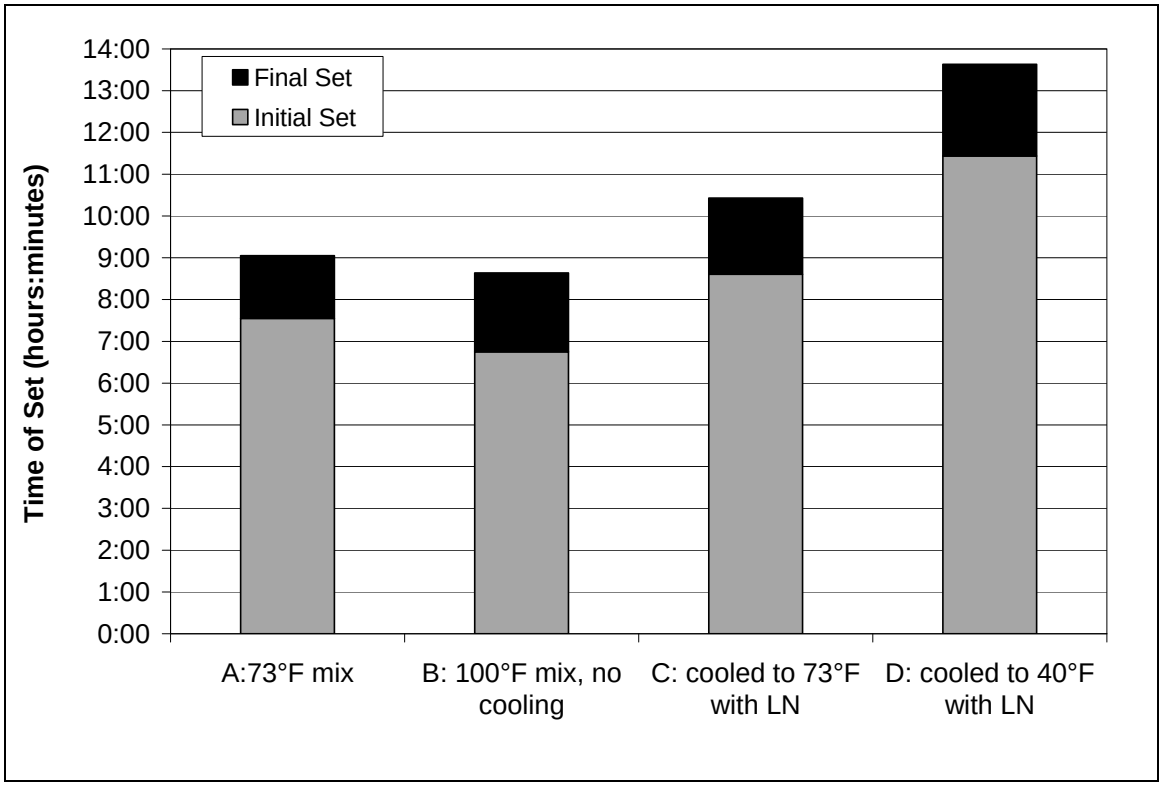


FIGURE 3.16 Effect of temperature on the setting time of concrete

The initial and final set times for mixtures A and C were not significantly different. In fact, the precision statement in ASTM C 403 allows for a single operator error of no more than 23% for initial set and 16% for final set. The differences in setting times between mixtures A and C were 14% for initial set and 15% for final set. These results are similar to those found in setting time tests for laboratory mixtures in section 3.3.5.1. Parallel testing by Solt (2006) showed increases in setting time for LN-cooled specimens that were stored in conditions mimicking field conditions. As expected, the initial and final set times of mixture D were greatly increased by near-freezing temperatures. Therefore, overdosing a concrete mixture in the field could have significant construction and durability implications. Although the initial and final set times are extended with the use of LN and by low placement temperatures, the window of finishability between initial and final set remains relatively constant for the 73°F and the

100°F mixtures. As for the 40°F mixture, the window of finishability increased to over 2 hours 11 minutes, which is typical of a cold concrete mixture.

3.3.6 Concrete Yield

Concrete yield is a quality control calculation to ensure that owners are receiving the entire amount of concrete that was ordered. Yield is calculated by adding up the total weight of all materials batched and dividing it by the unit weight of the mixed concrete. The weight of all materials is typically shown on the delivery ticket or it can be provided by the ready-mix producer. Unit weight is determined by measuring the weight of a known volume of concrete in accordance with ASTM C 138, "Standard Test Method for Density (Unit Weight), Yield, and Air Content (Gravimetric) of Concrete" the container for which is shown in Figure 3.17 (ASTM C 138, 2001). The calculation provides a volume that should match the amount of concrete that was ordered. If the yield is less than the amount of concrete ordered, then the producer is not providing the entire amount of concrete. A yield volume that is greater than the volume of concrete ordered means that the producer is providing more than the customer requested. To ensure that customers are not cheated, concrete producers usually over-yield by 0.5%. The yield calculation is effective for ensuring that the customer is satisfied with the amount of concrete they are receiving and that producers are providing just enough to maximize profits.

FIGURE 3.17 Measure used in unit weight testing of fresh concrete

Cooling concrete with LN may adversely affect yield. The extremely cold temperatures of LN could cause a reduction in concrete volume by thermal contraction, thereby reducing yield. The purpose of the unit weight testing was to determine if concrete producers have to compensate for any volume changes that occur when dosing concrete with LN. Unit weight measurements were taken for all concrete mixtures shown in Table 3.5 and then used to calculate the yield of both control and LN mixtures, as shown in Table 3.8. The percent change was calculated to determine the extent of volume change in LN mixtures compared to control mixtures. A negative percent change represents a volume decrease in LN mixtures compared to control mixtures, while a positive change represents a volume increase in LN mixtures.

3.3.6.1 Results and Discussion of Yield Calculation

The results of yield testing in 3.8 show small volume changes in concrete cooled with LN. Most of the mixtures experienced a volume reduction of no more than 2%. Only 4 of the mixtures had a volume reduction greater than 2%, with 4.8% being the

maximum. In fact, 2 of LN mixtures experienced a volume increase. Since no precision criterion exists for yield, it is difficult to determine if the results are significant. Since the differences in yield are so small between the control and LN-cooled mixtures, and the differences are both positive and negative for the mixtures tested, it can be safely assumed that concrete yield will not be affected when LN is used for cooling.

TABLE 3.8 Concrete Yield for Control and Liquid Nitrogen Mixtures

Mixes	**Yield (yd^3) Control Mixes**	**Yield (yd^3) LN Mixes**	**% difference in yield**
01	1.02	1.02	-0.1%
02	1.04	1.01	-2.2%
03	1.03	1.02	-1.6%
04	1.02	1.02	-0.1%
05	1.04	1.03	-1.5%
06	1.02	1.03	0.8%
07	1.02	1.01	-0.9%
08	1.05	1.04	-1.4%
09	1.07	1.03	-3.3%
10	1.03	1.02	-0.7%
11	1.04	1.03	-1.1%
12	1.02	1.02	-0.3%
13	1.02	1.02	-0.4%
14	1.02	1.02	-0.1%
15	1.03	1.02	-1.1%
16	1.06	1.04	-2.0%
17	1.09	1.04	-4.8%
18	1.06	1.07	0.6%
19	1.06	1.06	-0.6%
20	1.12	1.07	-4.2%

3.4 CONCLUSIONS

One major concern with the use of LN in concrete is the effect that it will have on fresh concrete properties, such as slump and setting time. Maintaining consistency in fresh concrete is already very difficult and dosing concrete with LN could increase the

difficulty in achieving the proper setting time and slump. Results from mortar flow testing indicated that LN has little effect on the flow of cement mortar. On the other hand, in laboratory testing, concrete slump appeared to decrease for LN-cooled concrete. However, further testing demonstrated that the slump loss was not caused by LN dosing but by preheating of the mixing materials. LN-cooled mixtures have similar slumps as mixtures with a fresh temperature similar to that of the initial material temperatures.

Setting time tests indicated that the use of LN to cool concrete did not have a significant effect on the initial or final setting time of concrete. Parallel testing by Solt (2006) showed increases in setting time for LN-cooled specimens that were stored in conditions mimicking field conditions. As well, the window of finishability, the time between initial and final set, remained unaffected in most cases. When concrete was cooled to 40°F, the window of finishability increased to over 2 hours 11 minutes, which is typical of a cold concrete mixture.

The results of yield testing show small volume changes in concrete cooled with LN. Most of the mixtures experienced a volume reduction of no more than 2%. It can be safely assumed that concrete yield will not be affected when LN is used for cooling.

CHAPTER 4: HARDENED PROPERTIES OF MORTAR AND CONCRETE

4.1 INTRODUCTION

The hardened properties of concrete control the serviceability of a structure. Concrete that is placed and cured properly forms a dense matrix that is highly resistant to both physical loads and chemical attack. Small errors in placement and curing could drastically shorten the service life of a structure or alter the hardened properties so much that the concrete cannot meet its intended function. A major concern with liquid nitrogen cooled concrete (LNCC) is the effect that liquid nitrogen (LN) has on the hardened properties of concrete. LN may reduce or increase the strength of concrete or could alter cement hydration to form a less dense or more dense microstructural network. These issues play a significant role in serviceability and durability. Furthermore, if the hardened properties of concrete are affected, it is vital to determine if the results are reversible or how to reverse the effects so serviceability is not impacted and durability is not compromised. This chapter deals specifically with mortar and concrete testing, which includes mortar compressive strength, and concrete compressive strength, splitting tensile strength, elastic modulus, and rapid chloride ion penetrability testing.

4.2 HARDENED PROPERTIES OF HYDRAULIC MORTAR

Compressive strength testing for 2–in. mortar cubes was performed according to ASTM C 109, "Standard Test Method for Compressive Strength of Hydraulic Cement Mortars" (ASTM C 109, 2007). Mortars were tested first as a "pilot" study in order to get quicker results and to gain a basic understanding of the effects of LN on compressive strength without having to make large concrete mixtures. This allowed for multiple mixtures to be made on a single day. Furthermore, the small mortar mixtures expedited the research by narrowing down the concrete testing matrix and by focusing the scope of the research.

4.2.1 Materials and Procedure

The materials used for the mortar consisted of TXI Type I/II cement from Hunter, Texas, manufactured sand from Austin Sand and Gravel in Southwest Austin, and distilled water. The fine aggregate used in mortar testing was a limestone-based river sand that was graded in accordance with ASTM C 33 (2007). An oxide analysis for the cement used in mortar testing is shown in Table 3.1 in Chapter 3.

The proportions of materials for each mixture were comprised of one part cement to 2.75 parts of graded fine aggregate with a water-to-cement ratio of 0.485. Three test specimens from each mixture were evaluated for compressive strength at 1-, 3-, 7-, and 28-days, bringing the total number of test specimens for each mixture to twelve. ASTM C 109 provides proportioning data for the molding of 6 specimens which was then doubled for this project in order to obtain the twelve necessary test specimens. The actual mixture proportions are as follows: 1.0 kg cement, 2.75 kg fine aggregate, and 242 mL water. Specimens were made using:

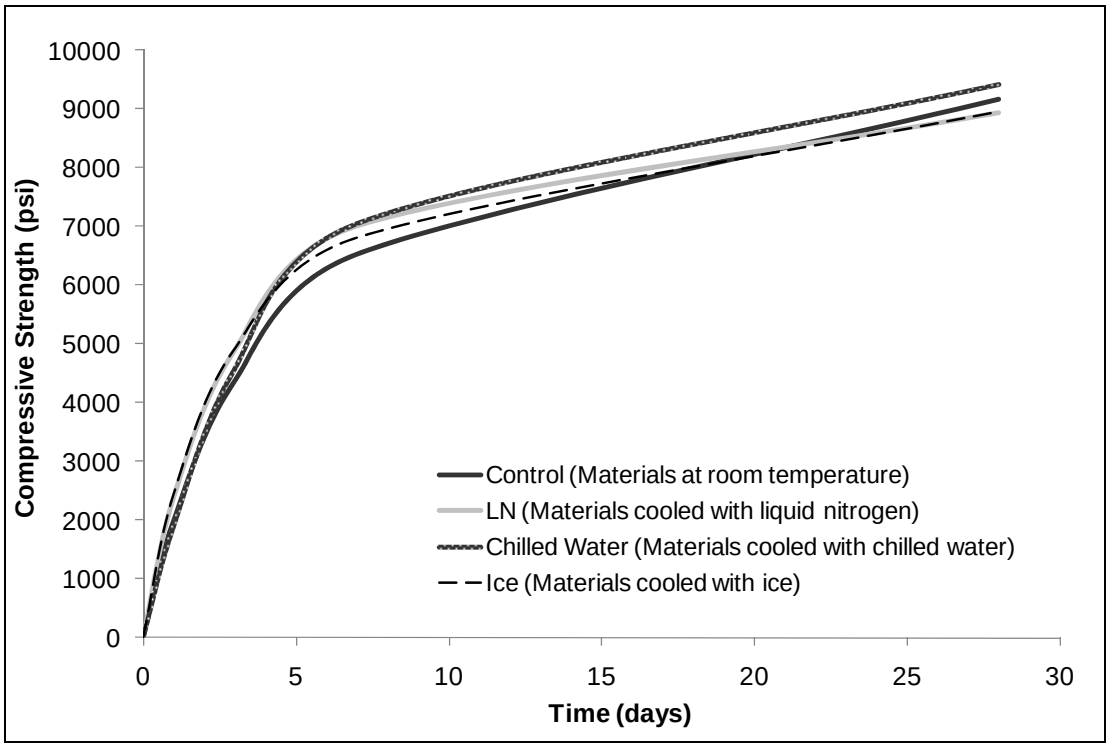
a. Ingredients at room temperature
b. Ingredients heated to 100°F and cooled to ~ 75°F using liquid nitrogen
c. Ingredients stored at 100°F and cooled to ~ 75°F using chilled water
d. Ingredients stored at 100°F and cooled to ~ 75°F using crushed ice

The admixtures used in the mortar mixtures consisted of two superplasticizers (Rheobuild 1000, BASF; and ADVA Flow, Grace), and two midrange water reducers (Pozzolith 961R and Pozzolith 200N, BASF).

Mortars were mechanically mixed in accordance with ASTM C 305, “Standard Practice for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency” (ASTM C 305, 2007). The paste was then tested for flow in accordance with ASTM C 1437 (2007). Immediately following the completion of the flow test, test specimens were molded into twelve 2–in. cubes. The mortar cubes were allowed to cure in a fog room at 73°F for 24 hours, after which time the mortar cubes were removed from the molds and returned to the fog room until testing.

4.2.2 Results

Figures 4.1 to 4.5 present compressive strength data for all mortar mixtures. Compressive strength data was collected at 1, 3, 7, and 28 days in order to generate the following figures. The graphs are categorized by admixture so that the effects of cooling method (LN, chilled water, or ice) on the compressive strength or the properties of the admixture are easily visible. These mixtures were replicated to ensure accuracy and the replicate data are in Appendix A.



F**IGURE 4.1** Compressive strength of mortar cubes containing no admixtures

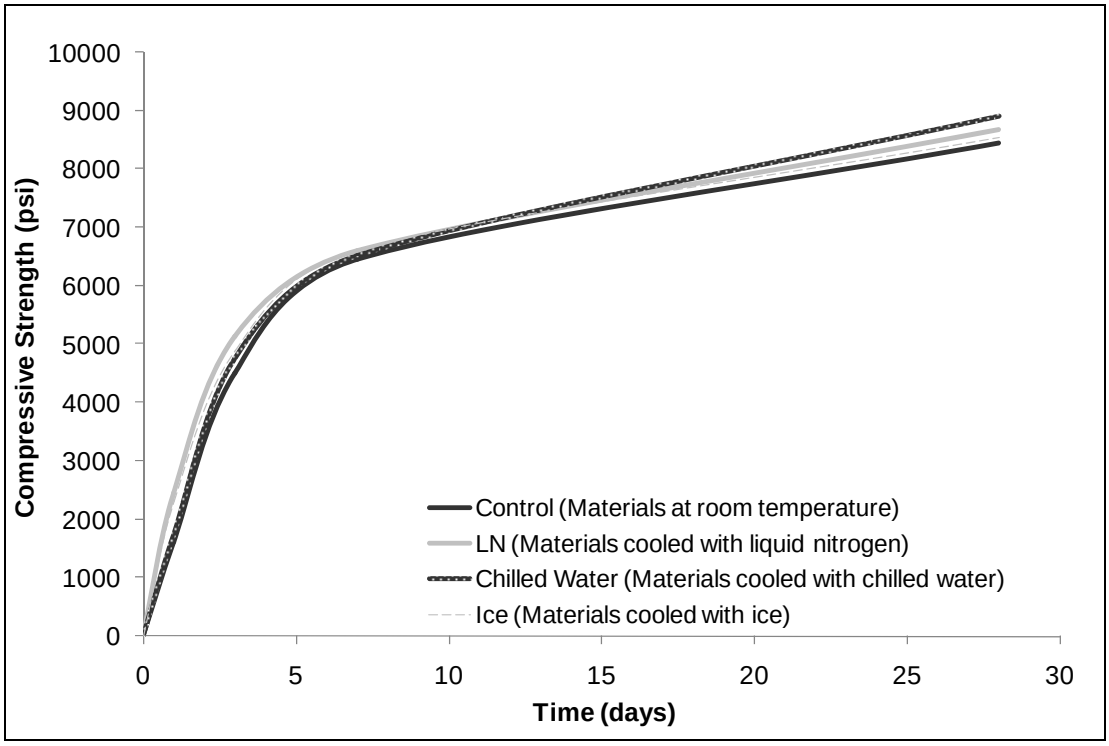


FIGURE 4.2 Compressive strength of mortar cubes containing Rheobuild 1000

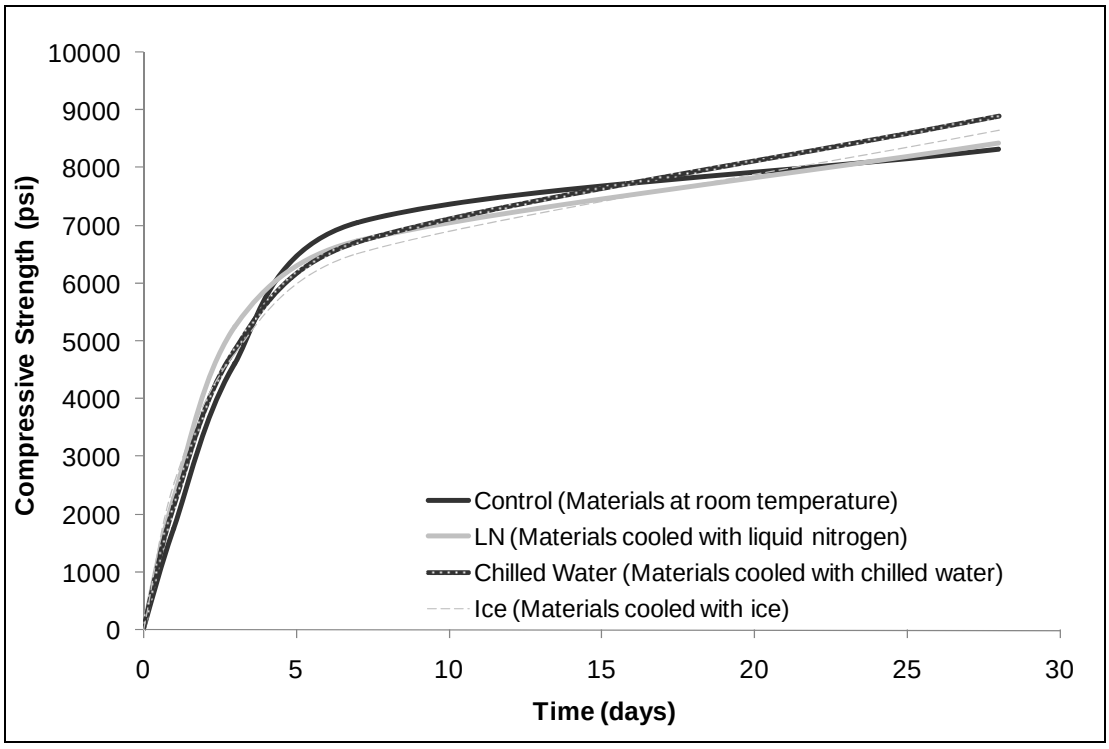


FIGURE 4.3 Compressive strength of mortar cubes containing ADVA Flow

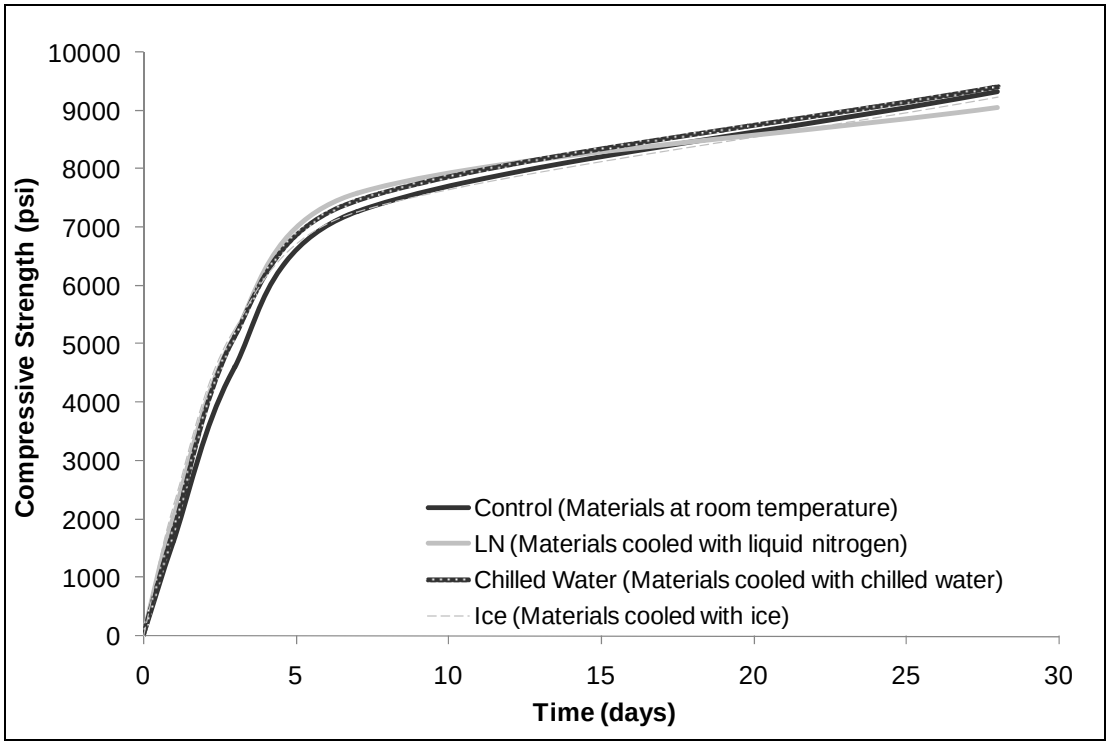


FIGURE 4.4 Compressive strength of mortar cubes containing Pozzolith961R

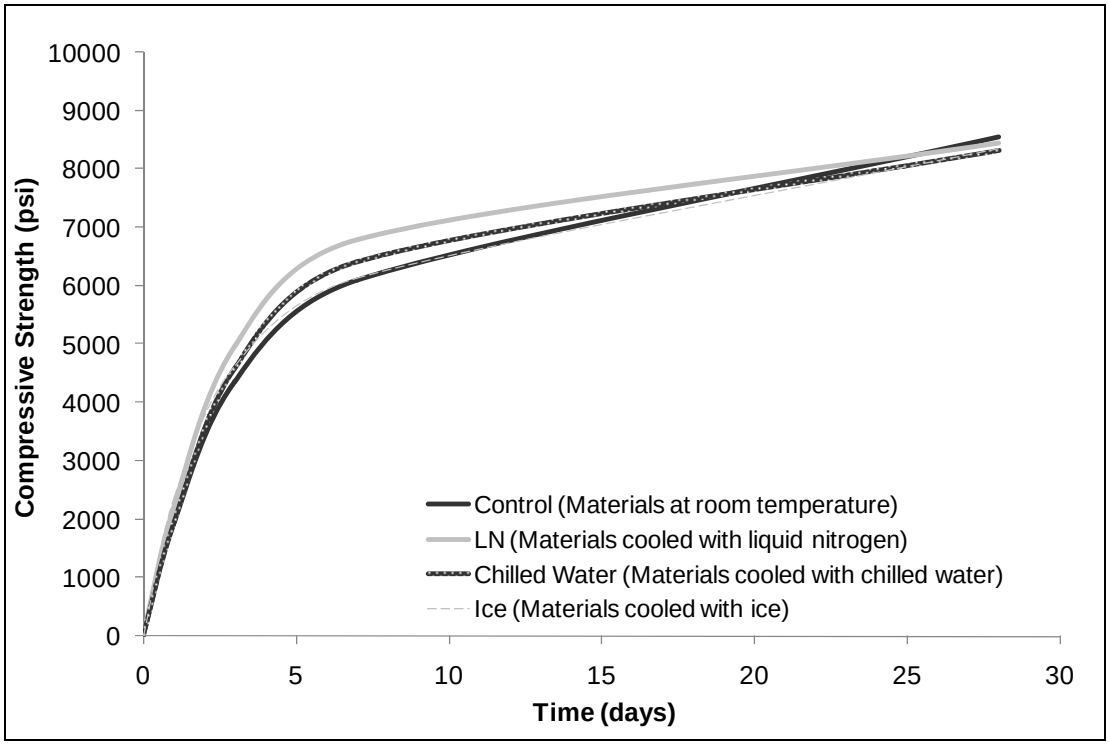


FIGURE 4.5 Compressive strength of mortar cubes containing Pozzolith 200N

4.2.3 Discussion

The data from Figures 4.1 to 4.5 show that LN does not affect the compressive strength of mortar mixtures made with or without chemical admixtures. The compressive strengths for cement mortar cooled with LN are comparable to the compressive strengths of the control, chilled water, and ice mixtures.

The precision statement in ASTM C 109 was used to determine significant changes in the compressive strength of the mortars. Since ASTM C 109 only gives precision data for 3 and 7 day mortar testing, the compressive strength for 28-day mortar testing was compared to the more stringent precision results, which is 10.2% for a single lab, 7-day mortar cube. Table 4.1 shows the difference in compressive strength in mortar cubes that used LN, ice, and chilled water compared to the control mortar cubes. A positive percentage indicates a higher compressive strength than the control mixture while a negative percentage indicates a lower compressive strength than the control mixture. The data in Table 4.1 show no significant changes in strength when using LN, ice, or chilled water. All of the mixtures remained under the 10.2% threshold. Therefore, the use of LN has no significant effect on the compressive strength of mortar cubes.

TABLE 4.1 Difference in 28-day Compressive Strength for Respective Cooling Methods

	Cooling Method		
	Liquid Nitrogen	**Chilled Water**	**Ice**
Mixes	*% difference in strength compared to control*		
No admixture	0.75%	6.34%	1.16%
Rheobuild 1000	2.58%	5.42%	1.11%
AdvaFlow	1.30%	6.75%	3.90%
Pozzolith 961R	-2.98%	0.74%	-1.20%
Pozzolith 200N	-1.25%	-2.62%	-2.19%

4.3 HARDENED PROPERTIES OF CONCRETE

As stated earlier, a major concern with LN cooled concrete is the effect that a cryogenic liquid has on the hardened properties of concrete. In particular, there are many

questions regarding the effect that LN has on strength. Compressive and splitting tensile strengths are the only concrete properties that are included in structural design calculations which make the result of this section important if LN does indeed affect strength. LN may considerably reduce or increase the strength of concrete

4.3.1 Concrete Materials

Concrete materials were procured through a variety of sources. The materials are representative of those used by Transit Mix Concrete and Materials Company in Austin for TxDOT mass concrete applications. A list of the materials, material types, and suppliers are shown in Chapter 3 in Table 3.2. In addition, a cement oxide analysis is shown for the TXI Type I/II cement in Table 3.3 and aggregate gradations and properties are shown in Table 3.4, also in Chapter 3.

4.3.2 Concrete Experimental Matrix and Mixture Design

The concrete testing matrix for hardened properties is the same as that for fresh properties and is shown in Chapter 3, in Table 3.5. It was developed to incorporate supplementary cementing materials (SCMs) and chemical admixtures that may be found in hot weather concreting and mass concrete applications. In addition, combinations of SCMs and chemical admixtures were tested to determine if LN would affect them differently when combined.

The concrete mixture design is the same as that used for testing fresh properties and is shown in Table 3.6. These are typical proportions for a one cubic yard concrete mixture. When SCMs were used, a certain percentage of cement was replaced with the same percentage of SCM, thereby maintaining the cementitious content and water-cement ratio. Each concrete mixture was used to make 27 - 4”x 8” cylinders, 2 – 6”x12” cylinders, and one Chinese take-out box (for hardened air void testing) with the following dimensions: 4.75 in. long, 3.75 in. wide and 4.00 in. high. Results from testing were compared between batches where all materials were at room temperature (73°F) to those where ingredients were stored at 100°F and cooled to room temperature using LN.

4.3.3 Concrete Mixing Procedure

The concrete mixing procedure is described in section 3.3.3.

4.3.4 Compressive Strength

The compressive strength is the most common performance parameter used by engineers in the design of structures. Compressive strength results are primarily used to ensure that a concrete mixture meets the design strength specified by the engineer. Strength testing may also be used for quality control to verify the accuracy of mixture proportions, to schedule formwork removal, or to determine when to proceed with subsequent phases of a project. Since concrete strength is heavily dependent on cement hydration, LN dosing may affect the rate at which concrete gains strength.

Compression testing of concrete is performed on concrete cylinders that are fabricated from a concrete mixture. The cylinders are made and cured in accordance with procedures found in ASTM C 31, "Standard Practice for Making and Curing Concrete Test Specimens in the Field" (ASTM C 31, 2003). Cylindrical specimens are tested in accordance with ASTM C 39, "Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens" (ASTM C 39, 2004), as shown in Figure 4.6. Testing is conducted at various days to monitor the strength gain over time. The most important test occurs at 28-days, which is the strength that is used in design calculations and to ensure that the target strength was achieved. According to ACI 318, "Building Code Requirements for Reinforced Concrete," concrete is considered acceptable as long as no single test is more than 500 psi below the design strength and the average of three consecutive tests equals or exceeds the design strength (ACI 318, 2005).

Compressive strength testing was performed on the 20 different concrete mixtures shown in Table 3.5. The research presented in this section compares compressive strength results between concrete batches where all materials were at 73°F to identical mixtures where ingredients were stored at 100°F and cooled to 73°F using LN.

FIGURE 4.6 Compressive strength testing of a concrete cylinder

4.3.4.1 Results of Compressive Strength Testing for Laboratory Mixed Concrete

Data presented in Figure 4.7 show that the 28-day compressive strengths for LN cooled concrete were greater in all cases but 2. For some mixtures, the difference between the control and the LN mixtures is quite dramatic. ASTM C 39 states that tests results of the same batch should not differ by more than 7.8%, which will be the threshold that identifies statistically significant results in compressive strength.

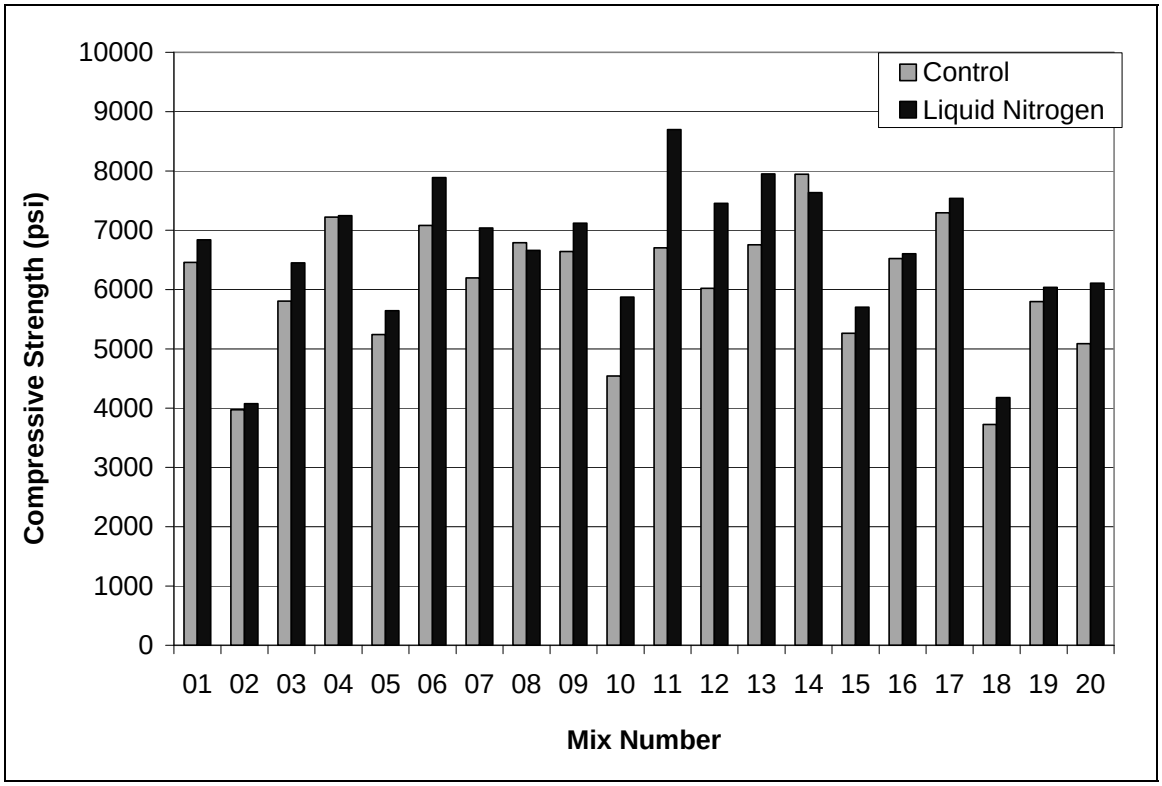


FIGURE 4.7 28-day compressive strengths for laboratory-mixed concrete

Table 4.2 shows the percent difference in 28-day compressive strengths between LN mixtures and control mixtures. A positive percentage signifies that the LN mixture has a higher compressive strength than the control mixture. Conversely, a negative percentage indicates that the LN mixture has a lower compressive strength than the control mixture. Numbers in bold denote that the mixture has exceeded the precision threshold in ASTM C 39. The compressive strength of concrete made with LN is significantly higher than that of concrete mixtures made without the use of LN. Table 4.2 shows that 50% of LN cooled mixtures showed significant strength gains.

TABLE 4.2 Difference in 28-day compressive strengths for laboratory-mixed concrete

Mix	**Difference in Compressive Strength**
	% difference between control and LN mixes
1	5.9%
2	2.6%
3	**11.1%**
4	0.3%
5	7.7%
6	**11.4%**
7	**13.6%**
8	-1.9%
9	7.2%
10	**29.3%**
11	**29.8%**
12	**23.8%**
13	**17.7%**
14	-3.9%
15	**8.4%**
16	1.3%
17	3.4%
18	**12.1%**
19	4.1%
20	**20.1%**

Additional compressive strength data for 1-day and 7-day tests are shown in Appendix B. The compressive strength results for 1-day and 7-day tests are consistent with those from 28-day testing. That is, concrete cooled with LN has higher compressive strengths than control mixtures. The compressive strength results for both early-age and 28-day testing are not consistent with exothermic reactions that occur during cement hydration. Cement reactions are accelerated by high curing temperatures and slowed by low curing temperatures. It was expected that the compressive strengths for LN cooled concrete would be lower than the control mixtures even though the LN mixtures were cooled to the same temperature as the control mixtures. In fact, the LN mixtures are

stronger than the control mixtures. Results for 1-day and 7-day compressive strength data are significant in 14 out of 20 mixtures and 16 out of 20 mixes, respectively. Nevertheless, there is no trend that suggests any differences in early-age strength of concrete cooled with LN.

Additionally, there is a general strength inversion that occurs with high and low temperature curing that may exist with concrete cooled with LN. Concrete cured at low temperatures is generally weaker at early-ages and stronger at later ages. The converse is true for high temperature curing. There is no evidence in the compressive strength data that suggests a strength inversion for concrete cooled with LN. Most likely the strength inversion is specific to curing temperatures and not fresh concrete temperatures.

It should be noted that the compressive strength samples were made from concrete that was mixed in the laboratory and experienced water loss, as discussed in section 3.3.3. The observed increase in strength may therefore be a result of water loss during cooling. These results may only be relevant in laboratory testing and may not be experienced in commercially produced concrete. Therefore, testing was performed on covered and uncovered mixtures to see the effects of water loss on compressive strength.

Testing was conducted on two separate concrete mixtures, mixtures 6 and 10. Details about mixture materials and the mixing procedure are discussed in 3.3.4.1. It was expected that the compressive strength of the covered concrete mixtures (some water loss) should fall between the room temperature control mixture (no water loss) and the uncovered concrete mixture (more water loss).

Results of compressive strength testing on covered and uncovered concrete confirm that water evaporation is contributing to increases in compressive strength, as shown in Figure 4.8. As expected, the lowest compressive strength was exhibited by the control mixture, which had the highest water-to-cement ratio since no water was lost to evaporation. The uncovered mixture had the highest compressive strength since it had the greatest amount of water loss resulting in a lower water-to-cement ratio. The compressive strength of the covered mixture was between the control and the uncovered mixture since water evaporation was reduced. Therefore, minimizing vapor loss will maintain the expected compressive strength of a concrete mixture.

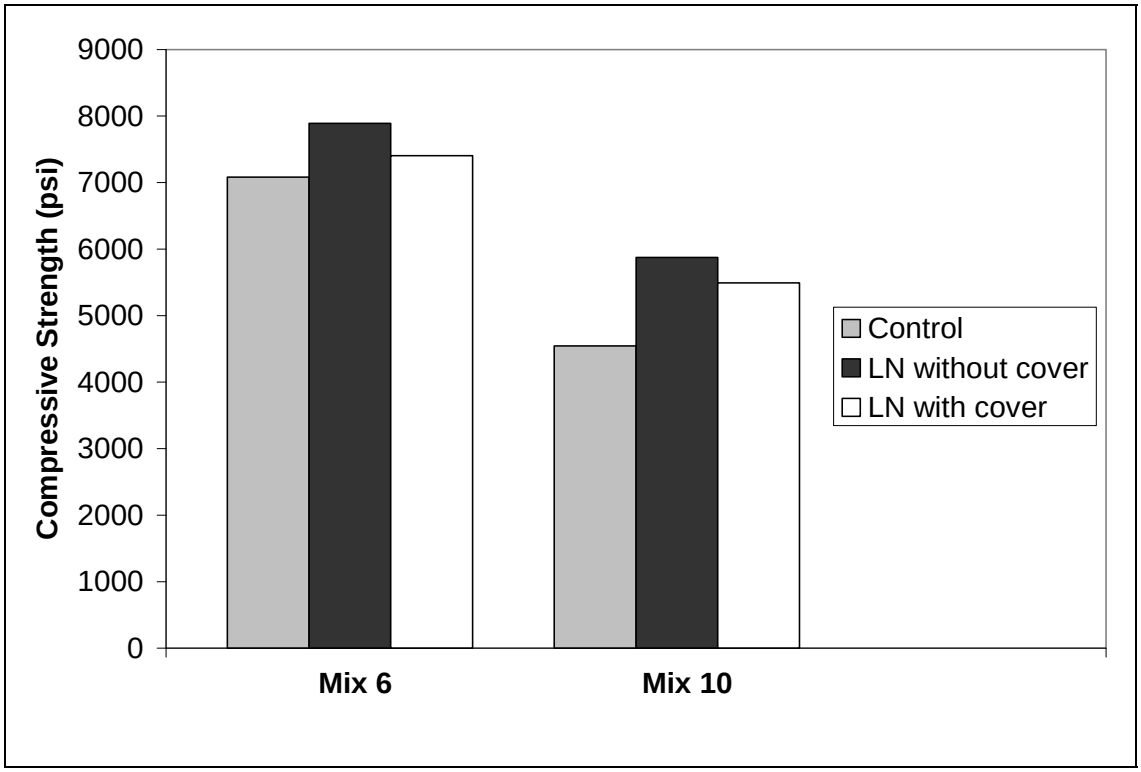


FIGURE 4.8 28-day compressive strengths of room temperature, covered, and uncovered concrete

A comparison of compressive strength data for mixtures 1-15 (uncovered) and mixtures 16-20 (covered) shows that covering the concrete mixer to reduce vapor emission did not considerably reduce the effect of LN on compressive strength. Mixtures 18 and 20 still showed significant strength gains even with the concrete mixer covered. It appeared that an unaccounted variable was causing increases in compressive strength. Further testing was conducted on field-mixed concrete to determine if increased compressive strengths were specific to laboratory mixed concrete.

4.3.4.2 Results of Compressive Strength Testing for Field Mixed Concrete

Field mixed concrete was sampled from concrete trucks at the Transit Mix batch plant in Round Rock, Texas. Sampling occurred in August 2006 on concrete that was to be used as slope stabilization for an open channel waterway. The exact composition of

the mixtures is unknown but they all contain Class F fly ash and a water reducer. Two wheelbarrows of concrete were taken from each ready-mix truck. The first wheelbarrow consisted of uncooled concrete that was between 93°F to 99°F. Cylinders were cast from these hot concrete mixtures and then moved into a climate controlled room that remained at 70°F. The second wheelbarrow consisted of cooled concrete that was between 65.1°F and 81.8°F. Once the cylinders were made, they were also moved into a climate controlled room where they cured for a day. The following day, the cylinders were stripped from their molds and placed in a curing room that is kept at 73°F with 100% relative humidity.

The 28-day compressive strength data for the field study are shown in Figure 4.9. Surprisingly, concrete cooled with LN was actually weaker in 75% of the mixtures than the concrete not cooled with LN. These data appear to contradict the results of laboratory testing. However, the differences in compressive strength between cooled and uncooled concrete for mixtures A-D are only -3.2%, 5.9%, -6.2%, and -0.6%, respectively. According to ASTM C 39, which states that tests results of the same batch should not differ by more than 7.8%, none of the differences in compressive strength are significant. Therefore, it appears that LN dosing had no affect on compressive strength for field mixed concrete.

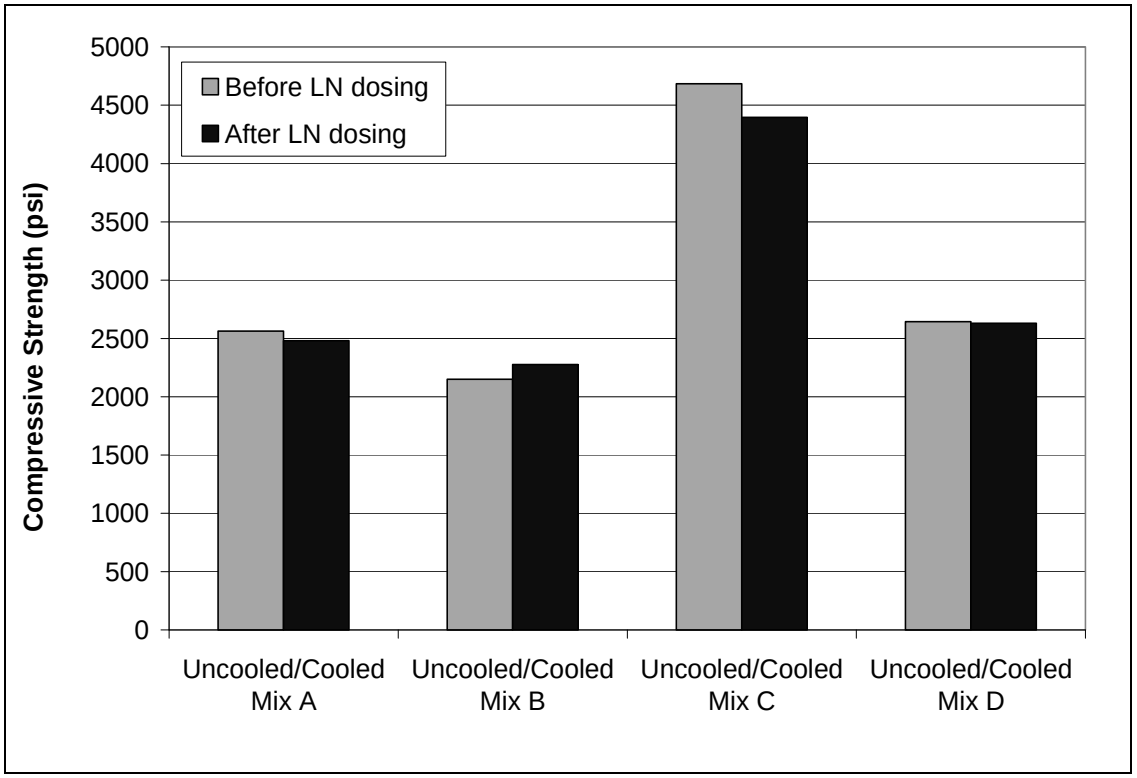


FIGURE 4.9 28-day compressive strengths for field-mixed concrete

4.3.4.3 Conclusions for Compressive Strength Testing

Compressive strength results at 28 days for laboratory-mixed concrete showed that, on average, the LN mixtures were 500 psi stronger than the control mixtures with 50% of the mixtures showing a statistically significant increase in strength. However, compressive strength testing of field-mixed concrete does not confirm the results of laboratory testing. For field mixtures, the compressive strengths for cooled and uncooled concrete were virtually the same. It is possible that this discrepancy is due to differences in the mixing procedures in the lab and in the field. Concrete mixed in the lab has a smaller volume, the relative size of the opening in the mixer is larger, and therefore experiences more water-loss during LN cooling, lowering the actual w/c and reducing strength. This strength loss should not be a concern in field concrete.

4.3.5 Splitting Tensile Strength

Splitting tensile strength is a mechanical property of concrete that is used in structural design. The direct application of tensile strength as a design parameter varies but is mainly used in the following design situations: shear strength and punching shear strength of slabs, bond anchorage, splicing of reinforcement, shear transfer in cracks, and minimum reinforcement. Tensile strength is equally important for unreinforced concrete structures that lack steel reinforcement to carry the tensile loads. As is the case with concrete compressive strength, splitting tensile strength is heavily dependent on cement hydration and may be affected by dosing fresh concrete with LN.

Testing for splitting tensile strength is conducted in accordance with ASTM C 496, "Standard Test Method for Splitting Tensile Strength of Cylindrical Concrete Specimens" (ASTM C 496, 2004). The test method consists of applying a compressive load along the length of a cylindrical concrete specimen until failure occurs, as shown in Figure 4.10. This type of loading creates tensile stresses on the plane containing the applied load and compressive stresses immediately around the applied load. Tensile failure occurs since the specimen is in a state of triaxial compression, allowing it to withstand higher compressive forces than would be possible by a uniaxial compression test. Plywood strips are used to apply a uniform load along the entire length of the cylinder. The maximum load is divided by appropriate geometrical factors to obtain the splitting tensile strength.

FIGURE 4.10 Splitting tensile strength testing of a concrete cylinder

4.3.5.1 Results of Splitting Tensile Strength Testing for Laboratory Mixed Concrete

Data presented in Figure 4.11 show that the 28-day splitting tensile strengths for LN cooled concrete are greater in all cases except for 3 of the mixtures. However, the differences between the control and the LN mixtures are not significant in most cases. ASTM C 496 states that tests results of the same batch should not differ by more than 14.0%, which will be the threshold that identifies statistically significant results in splitting tensile strength. Table 4.3 shows the percent difference in 28-day splitting

tensile strength between LN mixtures and control mixtures. A positive percentage signifies that the LN mixture has a higher splitting tensile strength than the control mixture. Conversely, a negative percentage indicates that the LN mixture has a lower splitting tensile strength than the control mixture. Numbers in bold denote that the mixture has exceeded the precision threshold in ASTM C 496.

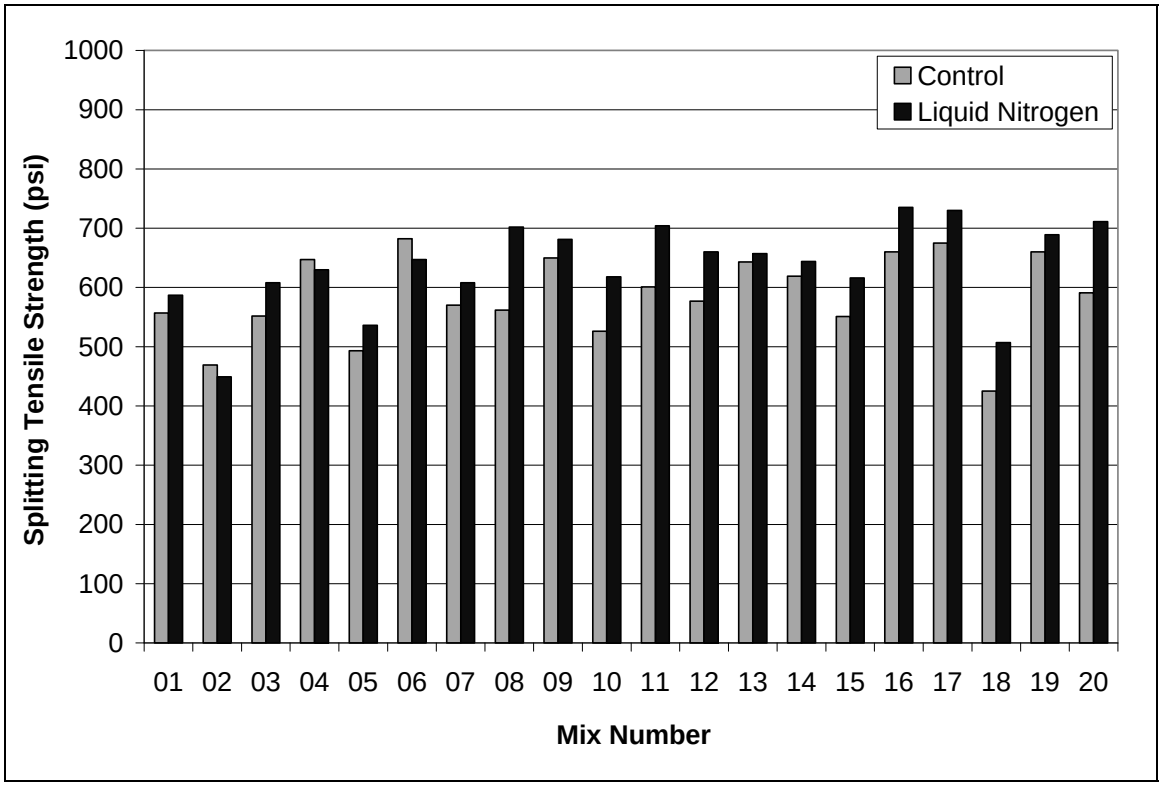


FIGURE 4.11 28-day splitting tensile strengths for laboratory-mixed concrete

The data in Table 4.3 show that only 30% of LN cooled mixtures experienced a statistically significant strength increase when compared to the control mixtures. A comparison of splitting tensile strength data for mixtures 1-15 (uncovered) and mixtures 16-20 (covered) shows that covering the concrete mixer to reduce vapor emission did not reduce the effect of LN on splitting tensile strength. Mixtures 18 and 20 still experienced significant strength gains even with the concrete mixer covered. To determine if these results were specific to laboratory mixed concrete, testing was

performed on concrete taken from several ready-mixed trucks on the same day that field testing was performed on compressive strength mixtures. Specific information concerning mixing materials and environmental conditions is shown in section 4.3.4.2.

TABLE 4.3 Difference in 28-day splitting tensile strengths of laboratory-mixed concrete

Mix	**Difference in Splitting Tensile Strength**
	% difference between control and LN mixes
1	5.4%
2	-4.3%
3	10.1%
4	-2.6%
5	8.7%
6	-5.1%
7	6.7%
8	**24.9%**
9	4.8%
10	**17.5%**
11	**17.1%**
12	**14.4%**
13	2.2%
14	4.0%
15	11.8%
16	11.4%
17	8.1%
18	**19.3%**
19	4.4%
20	**20.3%**

4.3.5.2 Results of Splitting Tensile Strength Testing for Field Mixed Concrete

The 28-day splitting tensile strength data for the field study are shown in Figure 4.12. Concrete cooled with LN was weaker than the concrete not cooled with LN in 75%

of the mixtures. However, the differences in compressive strength between cooled and uncooled concrete for mixtures A through D are -21.3%, -0.4%, -3.4%, and 3.3%, respectively. According to ASTM C 496, which states that tests results of the same batch should not differ by more than 14.0%, only the difference in splitting tensile strength for mixture A is considered statistically significant. However, the differences in splitting tensile data for 91 day testing are not significant. The differences at 91 days are -3.0%, -10.9%, 12.0%, and -6.2% for mixtures A through D, respectively. Therefore, it appears that the significant result for mixture A at 28 days is an outlier.

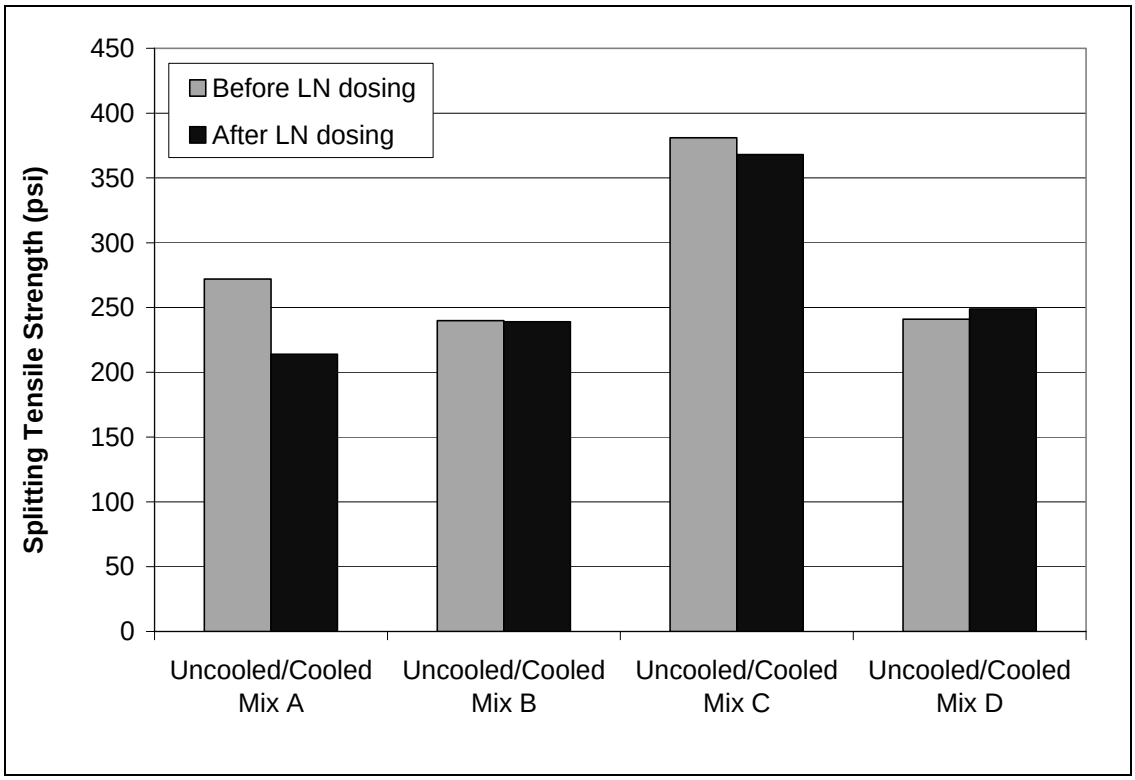


FIGURE 4.12 Splitting tensile strength for field-mixed concrete

4.3.5.3 Conclusions for Splitting Tensile Strength Testing

Splitting tensile results in laboratory mixed concrete showed that mixtures cooled with LN generally had higher splitting tensile strengths than control mixtures. Based on

the precision data in ASTM C 496, the differences in results were significant in only 30% of the mixtures. In field-mixed concrete, the differences between cooled and uncooled concrete were not statistically significant. As in the case of the compressive strength data, it is likely that the increase splitting tensile strength is due to water loss in the laboratory mixtures, a problem that is not relevant in the field.

4.3.6 Modulus of Elasticity

The modulus of elasticity is a measure of stiffness having the same units as stress (psi). Hooke's law states that stress is directly proportional to strain and therefore the ratio of the two is a constant that is commonly used to indicate the elasticity of a substance. Modulus of elasticity (*E*) is a key factor for estimating the deformation of buildings and members, such as to predict the load at which a thin column will buckle under compression. It is also a fundamental factor for sizing reinforced and unreinforced structural members and for determining reinforcement quantities. Factors that affect concrete strength also affect the modulus of elasticity. Therefore, the effects of LN on elastic modulus should be similar to the effects on compressive and splitting tensile strength.

Elastic modulus testing is conducted in accordance with ASTM C 469, “Standard Test Method for Static Modulus of Elasticity and Poisson's Ratio of Concrete in Compression” (ASTM C 469, 2002), on a 28-day cylinder mounted with a compressometer, as shown in Figure 4.13. The cylinder is loaded twice to 40% of ultimate strength (determined from previous testing of 2 companion cylinders) to ensure that the compressometer is seated properly. Testing is then performed on the cylinder by loading at a constant and continuous rate. Strain and load measurements are recorded when the longitudinal strain reaches 0.000050 and when the applied load is equal to 40% of the ultimate load. Additional readings may be taken to construct a stress versus strain plot for concrete in compression. To calculate *E,* the load is converted to stress by dividing the load by the cross-sectional area of the cylinder. *E* is then calculated by dividing the change in stress by the change in strain.

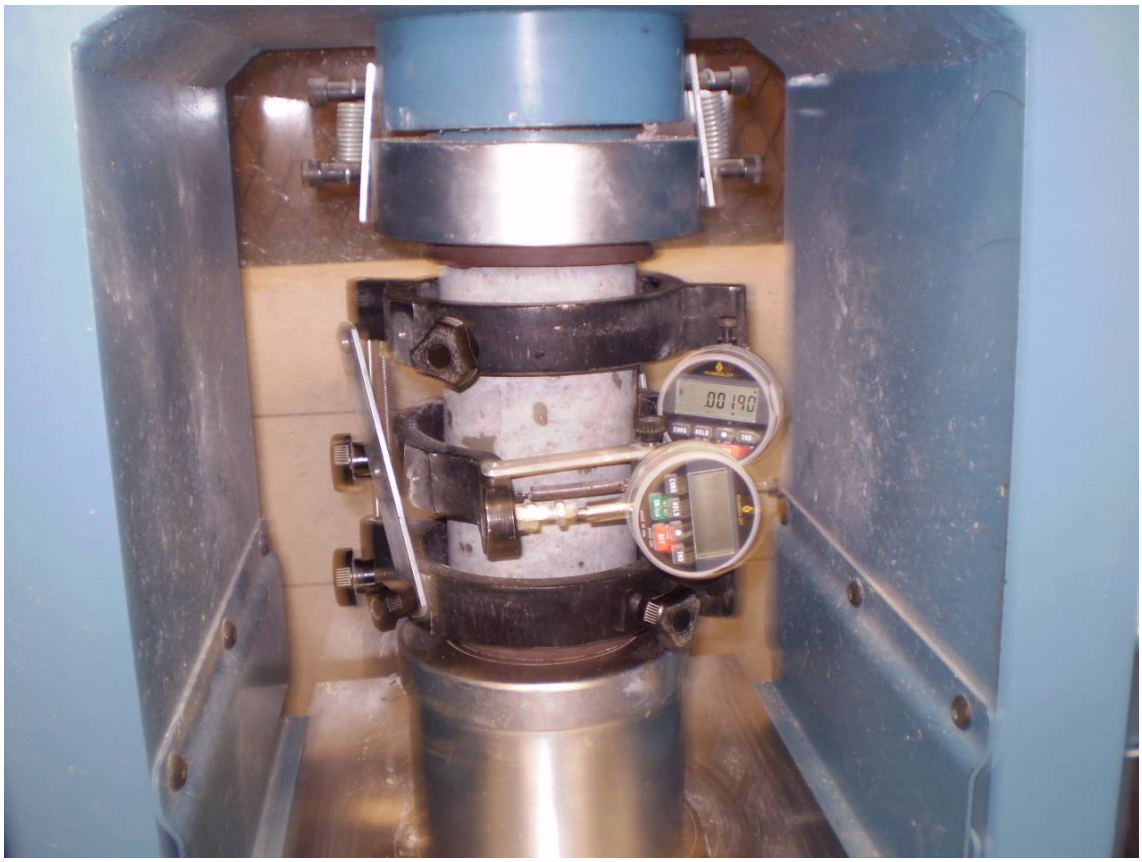


FIGURE 4.13 Elastic modulus testing of a concrete cylinder

4.3.6.1 Results of Elastic Modulus Testing

The data presented in Figure 4.14 give mixed results as to the effect of LN on elastic modulus testing. Approximately 56% of the LN mixtures had a higher elastic modulus than the controls, while 44% of the LN mixtures were lower. The elastic modulus of LN cooled mixtures should be proportional to strength values; that is, as strength increases, so should elastic modulus. Results of strength testing suggest that the elastic moduli of LN cooled concrete should be statistically higher in 50% of the mixtures. Only 18 mixtures were completely tested for elastic modulus since modulus specimens for mixtures 03 and 15 were damaged.

ASTM C 469 states that testing results should not differ by more than 5%, which will be the threshold that identifies statistically significant results in elastic modulus

testing. Table 4.4 shows the difference in 28-day elastic modulus testing between LN mixtures and control mixtures. A positive percentage signifies that the LN mixture has a greater elastic modulus than the control mixture. Conversely, a negative percentage indicates that the LN mixture has a lower elastic modulus than the control mixture. Numbers in bold denote that the mixture has exceeded the precision threshold in ASTM C 469.

The results presented in Table 4.4 are unclear with regards to the effect that LN has on elastic modulus. Similar to compressive strength testing, 50% of the mixtures showed statistically significant differences in the elastic modulus between LN cooled concrete and normal concrete. But, of those mixtures, some of the LN mixtures had a higher elastic modulus and others had a lower elastic modulus. The results of elastic modulus testing are unclear because there is not a well defined trend in the data.

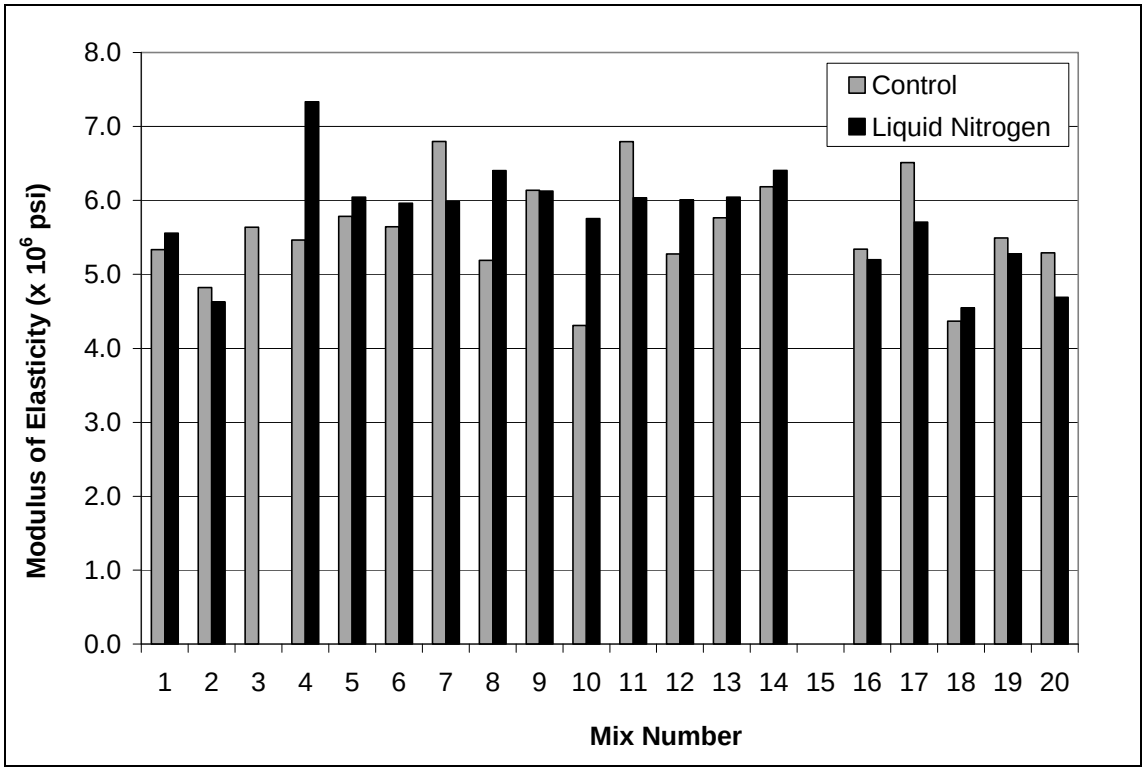


FIGURE 4.14 Modulus of elasticity comparison for control and liquid nitrogen mixtures

TABLE 4.4 Difference in Elastic Modulus for Control and Liquid Nitrogen Mixtures

Mix	**Difference in Elastic Modulus**
	% difference between control and LN mixes
1	4.1%
2	-4.0%
3	0.0%
4	**34.2%**
5	4.4%
6	**5.6%**
7	**-12.0%**
8	**23.3%**
9	-0.2%
10	**33.5%**
11	**-11.2%**
12	**13.8%**
13	4.8%
14	3.6%
15	0.0%
16	-2.7%
17	**-12.4%**
18	4.1%
19	-4.0%
20	**-11.4%**

4.3.6.2 Conclusions for Elastic Modulus Testing

The elastic modulus of LN cooled mixtures should be proportional to strength testing; that is, as strength increases, so should elastic modulus. Based on results from strength testing, it was expected that the elastic modulus for LN cooled concrete would be statistically higher than room temperature concrete mixtures in 50% of the cases. Indeed, 50% of the mixtures in Table 4.4 showed statistically significant differences in the elastic modulus between LN cooled concrete and normal concrete. But, of those mixtures, some of the LN mixtures had a higher elastic modulus and others had a lower

elastic modulus. The results of elastic modulus testing are unclear because there is not a well defined trend in the data.

4.3.7 Rapid Chloride-Ion Penetrability

Low-permeability concrete generally possesses high strengths and is resistant to the ingress of water and chlorides. Conversely, extremely porous concrete allows water, chlorides, and oxygen to more easily reach the reinforcing steel, which accelerates corrosion of the reinforcement. The rate of chloride ion ingress into concrete is primarily dependent on the internal pore structure, which is influenced by factors such as mixture design, degree of hydration, curing conditions, use of supplementary cementitious materials, and construction practices. LN dosing of fresh concrete may affect the internal pore structure of hardened concrete, possibly accelerating the ingress of chlorides. Measuring the chloride penetration of LN cooled concrete reveals the effects of LN on the permeability of hardened concrete.

The Rapid Chloride Penetrability Test (RCPT), ASTM C 1202, "Electrical Indication of Concrete's Ability to Resist Chloride Ion Penetration," is a method that indirectly measures concrete permeability (ASTM C 1202, 1997). The RCPT method is performed on concrete cylinders 4 inches in diameter and 2 inches in thickness. One side of the specimen is immersed in NaCl solution, while the other side is immersed in a sodium hydroxide solution (NaOH), as shown in Figure 4.15. An electrical voltage of 60 V DC is then applied to the specimen to force the chloride ions to migrate into the concrete. Current readings are taken every 30 minutes during the 6-hour test and then plotted as a function of time. The area under the curve indicates the total charge passed, which is a measure of the resistance of the concrete to the diffusion of chloride ions. A high charge indicates a low resistance to chloride ions and poor quality concrete. Table 4.5 provides values that relate the charge passed to chloride-ion penetrability.

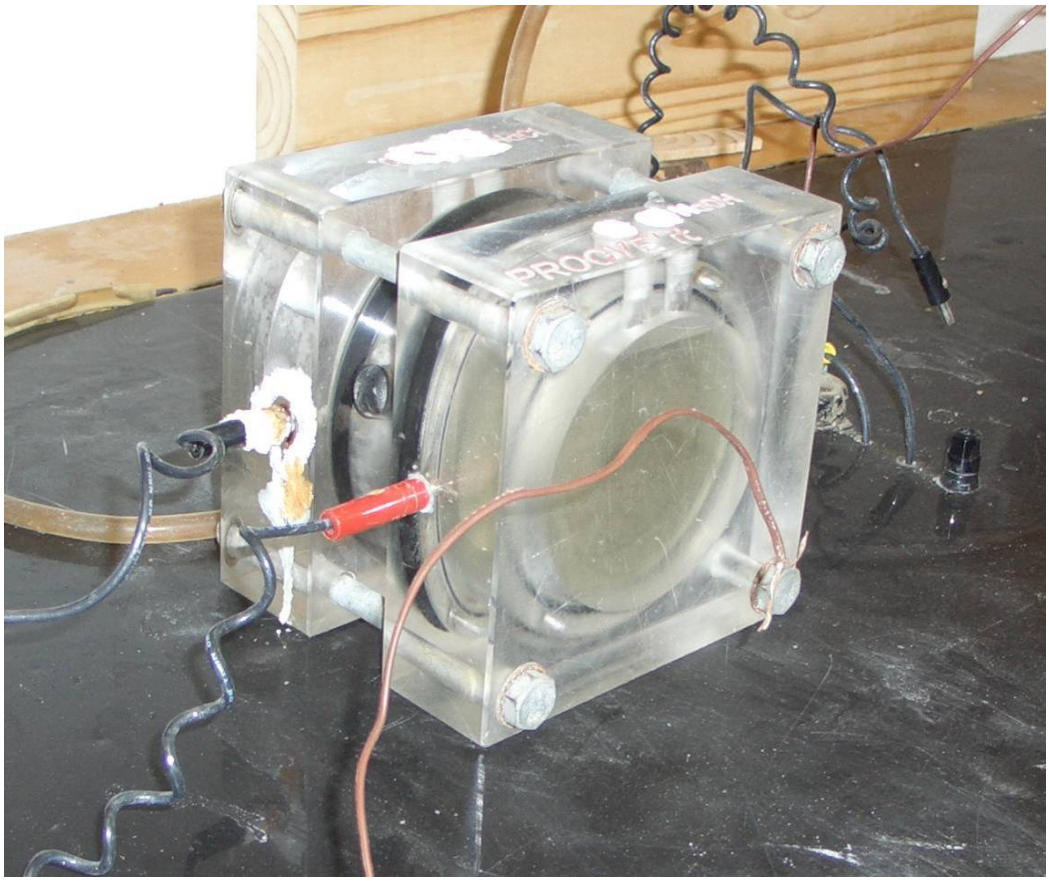


FIGURE 4.15 Rapid chloride penetrability test of concrete specimen

TABLE 4.5 Rapid Chloride-Ion Penetrability Ratings

Charge Passed (Coulombs)	**Chloride Ion Penetrability**
> 4,000	High
2,000 - 4,000	Moderate
1,000 - 2,000	Low
100 - 1,000	Very Low
< 100	Negligible

4.3.7.1 Results of Rapid Chloride-Ion Penetrability Testing

Data presented in Figure 4.16 show 90-day rapid chloride penetration results between room temperature mixtures and LN cooled mixtures. The electrical charge (Coulombs) that passed through LN cooled concrete was less for all cases except for 3 of the mixtures. ASTM C 1202 states that the results of two properly conducted tests by the same operator on concrete samples from the same batch may differ as much as 42%, which will be the threshold that identifies statistically significant results in RCP testing.

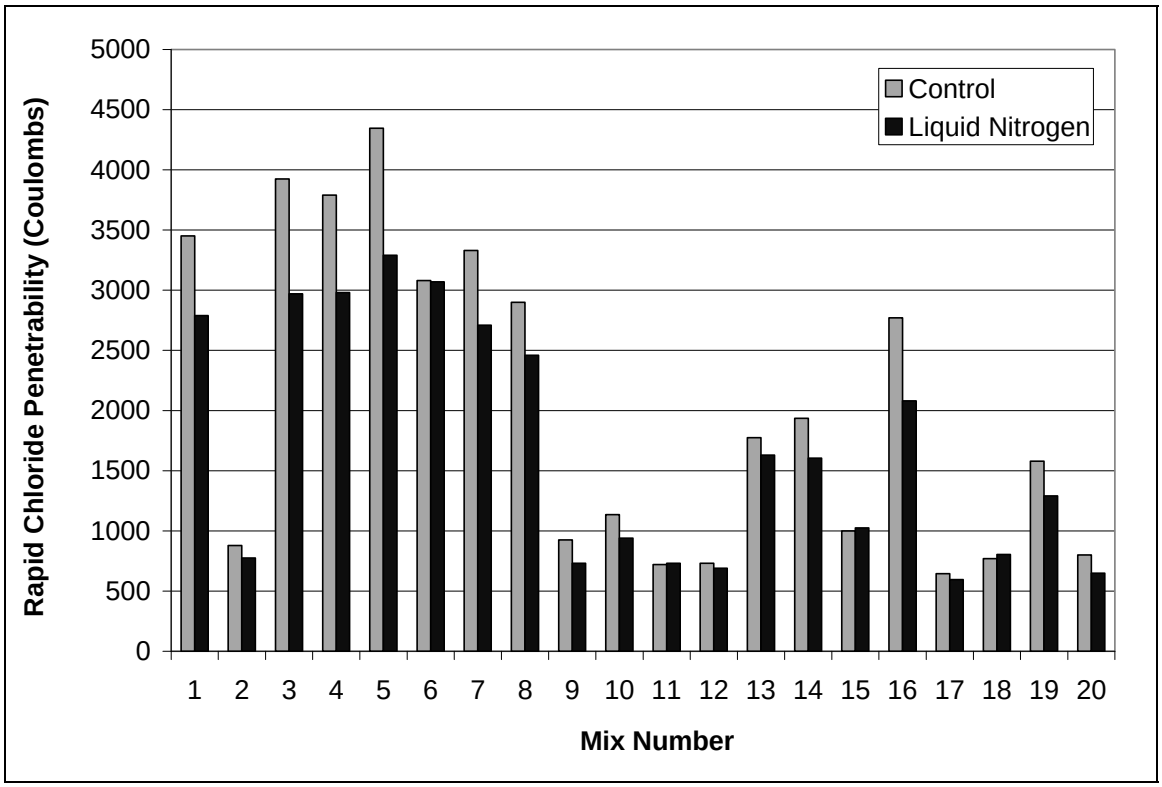


FIGURE 4.16 Rapid chloride penetrability data for control and liquid nitrogen mixtures

Table 4.6 shows the percent difference in the charge that is passed through LN and control mixtures. A positive percentage signifies that more charge is passed through the LN mixture, meaning that it is more permeable than the control mixture. Conversely, a negative percentage indicates that less charge is passed through the LN mixture, suggesting that it is less permeable than the control mixture. Since the precision

threshold is set so high (42%), none of the RCP tests give significant results. However, general trends will be surmised from the data.

In general, the data in Table 4.6 show that LN cooled concrete is less permeable than the control mixtures. The overall average change is -13.3% with a standard deviation of 10%. With regard to concrete permeability, a 13% reduction just by using LN could have a great impact on the ingress of harmful chemicals into concrete. Since none of the data are statistically significant, this trend should be noted, but more conclusive evidence is needed before accounting for it in concrete mixture design. As in the case of the compressive strength testing, it is possible that this reduction in permeability is due to water loss during cooling of laboratory mixtures and will not be relevant in the field.

4.3.7.2 Conclusions for Rapid Chloride-Ion Penetrability Testing

LN cooled concrete may be slightly less permeable than normal room temperature mixtures. Data from rapid chloride penetrability testing showed a 13.3% average reduction in the total electrical charge passed through LN cooled concrete, meaning that LN dosing created a denser concrete matrix. Based on data from strength and slump testing, the reduction in permeability is most likely caused by water evaporation during LN dosing. Even though the mouth of the concrete mixer was covered to prevent water loss, water vapor was free to escape out of the side of the cover since it was not completely air tight. Given the large threshold for statistical significance in this test (42%), none of the differences between LNCC and control mixtures are actually statistically significant. However, the trend is noted and may be the topic of future research.

TABLE 4.6 Rapid Chloride Penetrability Differences for Control and LN Mixtures

Mix	**Difference in Rapid Chloride Penetrability**
	% difference between control and LN mixes
1	-19.1%
2	-11.9%
3	-24.3%
4	-21.4%
5	-24.3%
6	-0.3%
7	-18.6%
8	-15.2%
9	-21.1%
10	-17.2%
11	1.4%
12	-5.5%
13	-8.2%
14	-17.1%
15	2.5%
16	-24.9%
17	-7.8%
18	4.5%
19	-18.4%
20	-18.8%

4.4 CONCLUSIONS

A major concern with LN cooled concrete is the effect that LN has on the hardened properties of concrete. LN may considerably change the strength of concrete or alter cement hydration and form a different microstructural network. These issues play a significant role in serviceability and durability.

The data presented in this chapter show that LN does not affect the compressive strength of mortar mixtures even with chemical admixtures. The compressive strengths

for cement mortar cooled with LN are comparable to the compressive strengths of the control, chilled water, and ice mixtures.

Compressive strength results at 28 days for laboratory-mixed concrete showed that, on average, the LN mixtures were 500 psi stronger than the control mixtures with 50% of the mixtures showing a statistically significant increase in strength. However, compressive strength testing of field-mixed concrete does not confirm the results of laboratory testing. For field mixtures, the compressive strengths for cooled and uncooled concrete were virtually the same. This discrepancy may be due to water loss during laboratory mixing and cooling conditions.

Splitting tensile results in laboratory mixed concrete showed that mixtures cooled with LN generally had higher splitting tensile strengths than control mixtures. Based on the precision data in ASTM C 496, the results were significant in only 30% of the mixtures. In field-mixed concrete, there were no statistically significant differences between cooled and uncooled concrete. Again, the higher strength of laboratory cooled concrete may be due to water loss on mixing.

The results of elastic modulus testing are unclear because there is not a well defined trend in the data. Statistically significant differences between cooled and uncooled samples were measured in 50% of the cases, but some were positive and some were negative.

Data from rapid chloride penetrability testing showed a 13.3% average reduction in the total electrical charge passed through LN cooled concrete. However, the threshold for statistically significant differences in this test is a 42% difference. The slight reduction in penetrability may be due to the same artifacts that increased strength, namely water loss in the laboratory mixer. A lower effective w/c could result in a slightly less penetrable concrete.

CHAPTER 5: EFFECTS ON CONCRETE CHEMISTRY AND HYDRATION

5.1 INTRODUCTION

Cement hydration is a chemical reaction that produces heat (exothermic). The natural progression of cement hydration involves the partial dissolution of cement grains and the reaction of individual ions with water to form hydration products that develop the dense matrix of concrete. The temperature at which cement hydrates controls the rate of reaction. Heat accelerates cement hydration. Conversely, cold temperatures slow down cement hydration reactions, causing a delay in the development of cement hydration products. Rapid hydration caused by high curing temperatures results in an irregular distribution of cement hydration products in the concrete microstructure (Chini et al., 2003; Kjellsen, 1996). In a high temperature environment, cement grains start to dissolve rapidly when brought into contact with water. A thin layer of hydration products initially develops around individual cement grains. When the reaction begins to accelerate, hydration products form rapidly both on the surface of the cement grain an in the solution between grains. The layer of hydration products on the cement grain becomes thick enough that the reaction slows down and becomes limited by the rate of diffusion of the ions through this layer. Under normal curing conditions, dissolved ions have sufficient time to diffuse into the space between cement grains and form a uniform microstructure. Under high temperature conditions, the rate of reaction is accelerated more than the rate of diffusion. Ions have less time to diffuse before reacting, resulting in denser hydration products immediately surrounding cement grains and less dense hydration products between grains. This microstructure is more heterogeneous and results in lower strength and higher permeability (Kjellsen, 1996). The permeability controls the rate at which deleterious chemicals penetrate into concrete. Therefore, durability can be increased by keeping the curing temperature of concrete relatively low to ensure that a uniform microstructure develops.

Liquid nitrogen (LN) shows a great deal of potential in lowering the placement temperature of fresh concrete. The use of LN would allow concrete producers to meet stringent temperature specifications without having to deal with partial water replacements with ice or chilled water. However, concerns arise over the use of liquid which is maintained at a temperature of -196°C (-320°F). Low placement temperatures prolong setting time and allow for better strength gain over time but freezing temperatures may cause ice crystals to form in concrete and prevent any further cement hydration in that local area. For this reason, testing was conducted to determine the effects of LN on the hydration and microstructure of cement. Testing included the use of semi-adiabatic calorimetry, isothermal calorimetry, x-ray diffraction (XRD), inductively coupled plasma (ICP), and environmental scanning electron microscopy (ESEM). Most testing occurred on concrete that was preheated to 100°F and cooled to 73°F with LN. Other tests were conducted on preheated concrete that was cooled to 50°F and 32°F. Another variable that was introduced into testing was delaying the dosing of LN for up to one hour for both calorimetry tests and up to 1 hour and 45 minutes for XRD and ICP. The goal of this portion of the research project was to ensure that the formation of ettringite, calcium hydroxide (CH), monosulfoaluminate (AFm), and calcium silicate hydrate (C-S-H) in LN mixtures develop in the same manner as normal room temperature mixtures.

5.2 SEMI-ADIABATIC CALORIMETRY

Processes that produce heat are referred to as exothermic and processes that consume heat are called endothermic. Calorimeters are used in concrete research to measure heat emission during the cement hydration process. Heat emission fluctuates widely during cement hydration due to the different rates of reactions of cementitious phases and different stages of the reaction process. By measuring heat emission over time, the cement hydration process can be monitored and any differences in the hydration process when using LN to cool cement pastes can be detected. Differences in heat evolution would provide evidence that LN dosing alters the hydration process.

Semi-adiabatic calorimetry was used for this research to compare the hydration development of LN-cooled concrete to control mixtures. In adiabatic calorimetry testing, the heat of hydration is measured by monitoring the temperature in a concrete specimen that is completely insulated to prevent any heat loss to the surrounding environment (Poole et al., 2007; Schindler and Folliard, 2005). For semi-adiabatic calorimetry, the specimen is also sealed and placed in a well-insulated chamber, but it allows for a small amount of heat loss to the environment (Wang et al., 2007). Thermocouples are used to measure the temperature of the concrete sample and the heat lost through the calorimeter insulation so that corrections can be made to back-calculate the temperature rise under fully adiabatic conditions. A theoretical adiabatic hydration curve can be calculated based on the temperature sensitivity (activation energy), total heat of hydration, and calibrated heat loss in the semi-adiabatic calorimeter.

Degree of hydration (α) is a quantitative value that indicates the hydration progress for portland cement. This value varies between 0 and 1, with a value of 1 indicating complete hydration. Degree of hydration is expressed as the ratio of heat evolved at time, *t*, to the total amount of heat available, as shown in Equation 5-1 (Poole et al., 2007):

$$\alpha = \frac{H(t)}{H_u} \qquad \text{Equation 5-1}$$

where α = degree of hydration at time *t*, *H(t)* = heat evolved from time 0 to time *t* (J/gram), and H_u = total heat available for reaction (J/gram).

H_u is defined in the following expression and is takes into consideration the amount and type of supplementary cementing materials (SCMs) as well as cement composition:

$$H_u = H_{cem} \cdot p_{cem} + 461 \cdot p_{slag} + 1800 \cdot p_{FA-CaO} \cdot p_{FA} \qquad \text{Equation 5-2}$$

where p_{slag} = slag mass to total cementitious content ratio, p_{FA} = fly ash mass to total cementitious content ratio, $p_{FA\text{-}CaO}$ = fly ash CaO mass to total fly ash content ratio, p_{cem} =

cement mass to total cementitious content ratio, and H_{cem} = heat of hydration of the cement (J/gram). H_{cem} can be calculated with the following expression in Equation 5-3:

$$H_{cem} = 500 \cdot p_{C_3S} + 260 \cdot p_{C_2S} + 866 \cdot p_{C_3A} + 420 \cdot p_{C_4AF} + 624 \cdot p_{SO_3} + 1186 \cdot p_{FreeCa} + 850 \cdot p_{MgO} \quad \text{Equation 5-3}$$

where H_{cem} = total heat of hydration of portland cement (J/gram) at α = 1.0, and p_i = mass of i-th component to total cement content ratio. A more detailed discussion of the calculation process is provided by Poole et al. (2007).

The semi-adiabatic calorimeter used in this study consisted of a well-insulated 55 gallon steel drum with an opening for a 6 x 12 in. concrete cylinder sample (Figure 5.1). Thermocouples were used to measure the temperatures in the concrete sample, the calorimeter insulation, and the air surrounding the calorimeter. Calibration testing was conducted on heated water to determine the heat loss through the calorimeter insulation. Samples consisted of 6 x 12 in. cylindrical concrete specimens identical to those commonly used in compressive strength testing. Once the concrete was mixed, a concrete sample was prepared and placed in the calorimeter for a period of 7 days (Poole et al., 2007; Schindler and Folliard, 2005).

FIGURE 5.1 Semi-adiabatic calorimeter

5.2.1 Experimental Methods for Semi-Adiabatic Calorimetry

Semi-adiabatic calorimetry testing was performed on 14 different concrete mixtures, each mixture consisting of a control and a LN sample. The concrete testing matrix for these tests is shown in Table 3.5 and was developed to incorporate supplementary cementing materials (SCMs) and chemical admixtures that may be found in hot weather concreting and mass concrete applications. In addition, combinations of SCMs and chemical admixtures were included to determine if LN would affect them differently when combined.

Each individual mixture was prepared twice so that a control and a LN mixture could be compared to each other. The control mixtures were comprised of mixing materials that were stored at 73°F, mixed at 73°F, and cured at 73°F. The LN mixtures were comprised of mixing materials stored at 100°F, mixed at 100°F, and then cooled to 73°F with LN after approximately 5 minutes of mixing. The mixing procedure is contained in section 3.3. It should be noted that some of the mixtures in Table 3.5 were not tested in the semi-adiabatic calorimeter due to instrument availability. Because of the availability of the calorimeter, mixtures 11, 12, 15, 16, 17, and 20 were not tested.

5.2.2 Results of Semi-Adiabatic Calorimetry Testing

The plot in Figure 5.2 shows degree of hydration versus time curves generated from semi-adiabatic calorimetry data for the control and LN samples of mixture 8 (air entrainer + water reducer). These curves were generated with the equations 5-1, 5-2, and 5-3. It appears that LN had no effect on the hydration for this particular mixture. These results were typical for almost all mixtures. Results for all mixtures are shown in Appendix C.

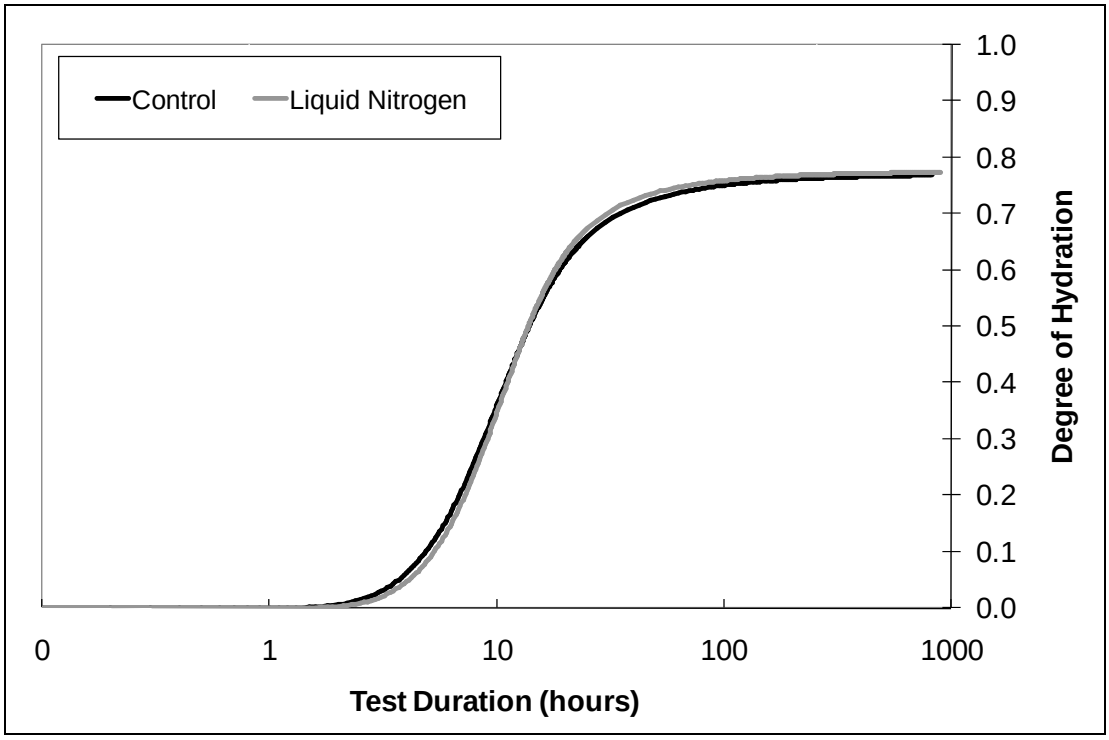


FIGURE 5.2 Degree of hydration curves from semi-adiabatic calorimetry for Mixture 8 (air entrainer + water reducer)

The results in Figure 5.3 show that LN did affect the hydration development for mixture 19 (C ash + polycarboxylate superplasticizer + air entrainer). This effect may have been caused by an interaction of the LN with the admixtures used, slowing the rate of heat development. It could also be the result of experimental error. The tests would have to be repeated and more work performed to confirm that this difference is real and discern the cause.

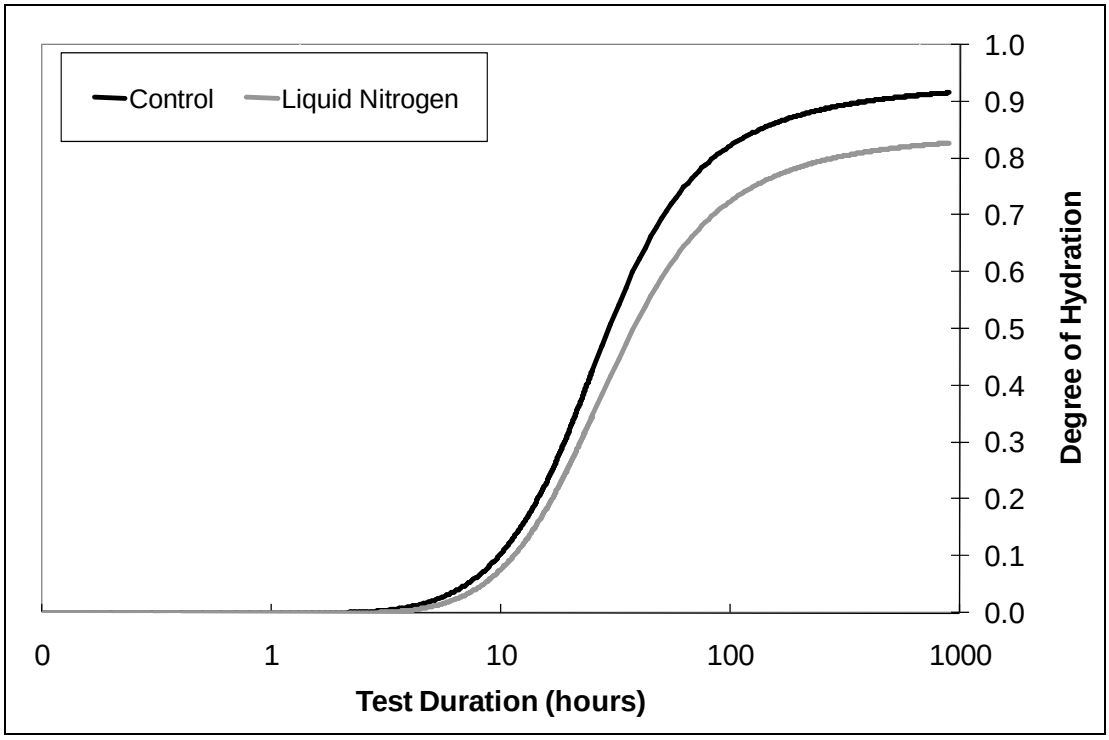


FIGURE 5.3 Degree of hydration curves for Mixture 19 (C ash + polycarboxylate superplasticizer + air entrainer)

The variability of the test results are quantified by comparing the variation in the curve fit parameters (α, β, and τ) for the 14 concrete mixtures, where τ = hydration time parameter (hours), β = hydration shape parameter, and α_u = ultimate degree of hydration. Precision testing on semi-adiabatic calorimeters used at the University of Texas at Austin showed that for any two test results, a difference of 8.8% for α_u, 20.9% for τ, and 16.9% for β is considered statistically significant at a 95% confidence level (Poole et al., 2007).

Table 5.1 shows the curve fit coefficients for each concrete mixture. The concrete samples are divided up by mixture comparing the control and LN samples to each other. For each curve fit parameter, the variation between control and LN samples was calculated. Bolded variation numbers highlighted indicate results that are statistically significant. Positive variation numbers indicate that the curve fit coefficient for the LN mixture is higher than the control while negative variation numbers indicate that the curve fit coefficient for the LN mixture is lower than the control.

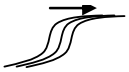
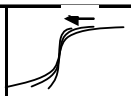
Based on the precision data in Table 5.1, it appears that LN has very little effect on the development of hydration of concrete samples. Results show that only four of the curve fit parameters for semi-adiabatic calorimetry data were considered statistically significant. None of the results that were considered statistically significant exceeded the precision threshold by more than 3.9% for α and 2.2% for β. In addition, no mixture had more than one curve fit parameter that was considered statistically significant.

A comparison of LN and control mixtures for α shows that LN dosing increases the ultimate degree of hydration in 57% of the mixtures and reduces the ultimate degree of hydration in 43% of the mixtures. Although the statistical analysis shows that two of the mixtures were considered statistically significant, it can be concluded that LN dosing has no effect on the ultimate degree of hydration of concrete mixtures.

A comparison of LN and control mixtures for τ shows that LN dosing extends the time parameter in 57% of the mixtures and reduces the time parameter in 43% of the mixtures. Based on precision data, it can be concluded that LN dosing has no effect on the time parameter of concrete mixtures.

A comparison of LN and control mixtures for β shows that LN dosing increases the hydration shape parameter in 86% of the mixtures and reduces the hydration shape parameter in 14% of the mixtures. The statistical analysis shows that two of the mixtures were considered statistically significant. It is likely that LN dosing has no effect on the shape of the hydration curve.

TABLE 5.1 Curve Fit Parameters for Concrete Mixtures

Mix ID	 α	% Diff	 τ	% Diff	 β	% Diff
C01 LN01	0.788 0.757	-4.01%	13.146 13.884	5.62%	0.797 0.823	3.31%
C02 LN02	1.000 1.000	0.00%	16.726 17.755	6.15%	0.690 0.722	4.76%
C03 LN03	0.794 0.733	-7.67%	14.084 16.549	17.50%	1.205 1.296	7.58%
C04 LN04	0.819 0.758	-7.46%	14.998 16.418	9.47%	0.978 1.145	**17.14%**
C05 LN05	0.776 0.806	3.80%	15.000 16.396	9.31%	0.898 0.875	-2.59%
C06 LN06	0.794 0.805	1.36%	14.905 14.111	-5.32%	0.851 0.914	7.44%
C07 LN07	0.746 0.786	5.36%	14.396 15.415	7.08%	0.936 1.016	8.55%
C08 LN08	0.802 0.808	0.78%	13.599 13.818	1.61%	0.850 0.900	5.85%
C09 LN09	0.935 0.830	**-11.24%**	32.742 28.823	-11.97%	0.584 0.640	9.50%
C10 LN10	0.854 0.963	**12.71%**	16.865 16.864	-0.01%	0.744 0.714	-3.98%
C13 LN13	0.953 0.873	-8.40%	29.864 25.925	-13.19%	0.695 0.771	10.90%
C14 LN14	1.000 0.932	-6.77%	30.354 29.092	-4.16%	0.664 0.684	3.06%
C18 LN18	0.857 0.786	-8.35%	17.299 17.663	2.10%	0.682 0.813	**19.13%**
C19 LN19	0.877 0.819	-6.67%	30.026 27.306	-9.06%	0.765 0.857	11.97%

5.3 ISOTHERMAL CALORIMETRY

Isothermal calorimetry can be used to measure the progress of the cement hydration reactions by measuring the heat produced in cement pastes kept at a constant temperature. Isothermal calorimetry data can be used to detect any differences in the hydration process when using LN to cool cement pastes. Differences in the heat evolution curve would provide evidence that LN dosing alters the hydration process.

For this research, a TAM Air (Thermometric) isothermal calorimeter was used to measure the amount of heat emitted during the hydration process of cement paste samples, as shown in Figure 5.4. The principle on which the calorimeter works is that heat generated during the chemical reaction flows rapidly through a thermal conductor to an aluminum heat sink which is maintained at a constant temperature by a surrounding air bath. A Peltier module and a temperature sensing probe keep the temperature of the sample constant at 23°C (73°F) by removing heat as it is generated. Incremental measurements are taken of the energy required to maintain the sample at 23°C.

5.3.1 Isothermal Calorimetry Experimental Matrix

The testing matrix in Table 5.2 was developed to incorporate supplementary cementing materials (SCMs) and chemical admixtures that may be found in hot weather concreting and mass concrete applications. The SCMs used in the mixing matrix were acquired from companies within Texas. Deely and Big Brown fly ashes are distributed by Boral Materials and produced in power plants in San Antonio, TX and Fairfield, TX, respectively. Parish and Martin Lake fly ashes are distributed by Headwaters Resources and produced in Thompsons, TX and Tatum, TX respectively. Slag was acquired from Holnam. Daracem 65, Daracem 19, ADVA Flow and Daratard 17 are all products produced by W.R. Grace. Pozzolith 200N is a product manufactured by BASF. An oxide analysis for the cement used in the subsequent tests is shown in Table 5.3.

FIGURE 5.4 TAM Air Isothermal Calorimeter

Isothermal calorimetry samples were prepared by mixing 250 grams of cementitious materials (cement and SCMs) with 110 grams of water. The materials were mixed in a kitchen blender for 10 seconds, after which the sides of the blender were scraped with a spatula to remove any cementitious material. The blender was then started again for another 20 seconds to complete mixing. Dosing of LN occurred during the final phase of mixing until the concrete was cooled to the proper temperature. At times, LN dosing required more than 20 seconds to complete.

Each mixture in Table 5.2 was made 4 times with different cooling criteria. By changing the time and duration of LN dosing, the effects of cryogenic temperatures on

fresh cement samples can be determined. Mixture A was chosen as the control mixture and provides a baseline curve by which all other experimental samples can be compared. Mixture B simulates current LN dosing procedures where hot concrete mixtures are cooled to a specified temperature immediately upon charging the mixer. Mixture C was chosen since TxDOT has specified a minimum concrete temperature of 50°F. Mixture D was chosen to see how delayed dosing of concrete would compare to the control mixture. The following is a list of the cooling group (A-D) and corresponding procedure:

A. Materials stored at 73°F, mixed at 73°F, tested at 73°F (the test actually runs at 23°C).
B. Materials stored at 100°F, mixed hot materials, cooled mixture to 73°F with liquid nitrogen, tested at 73°F.
C. Materials stored at 100°F, mixed hot materials, cooled mixture below 50°F with liquid nitrogen, allowed to warm to 73°F, tested at 73°F.
D. Materials stored at 100°F, mixed hot materials and let sit for 1 hour, cooled mixture to 73°F with liquid nitrogen, tested at 73°F.

TABLE 5.2 Testing Matrix for Isothermal Calorimetry Mixtures

Mix Number	Mix Description	Cement Type	SCM Type (% replacement)	Chemical Admixture (fl.oz per 100 weight cement)
1	Control	I/II	x	x
2	Slag	I/II	Slag (50%)	x
3	C Ash	I/II	Deely (30%)	x
4	C Ash	I/II	Parish (30%)	x
5	F Ash	I/II	Big Brown (20%)	x
6	F Ash	I/II	Martin Lake (20%)	x
7	Water Reducer (WR)	I/II	x	Pozzolith 200N (4.0)
8	Midrange Water Reducer (MRWR)	I/II	x	Daracem 65 (3.0)
9	Naphthalene Superplasticizer (Naph)	I/II	x	Daracem 19 (10.0)
10	Polycarboxylate Superplasticizer (Poly)	I/II	x	ADVA Flow (3.0)
11	Slag + WR	I/II	Slag (50%)	Pozzolith 200N (4.0)
12	Slag + MRWR	I/II	Slag (50%)	Daracem 65 (3.0)
13	Slag + Naph	I/II	Slag (50%)	Daracem 19 (10.0)
14	Slag + Poly	I/II	Slag (50%)	ADVA Flow (3.0)
15	C Ash + WR	I/II	Deely (30%)	Pozzolith 200N (4.0)
16	C Ash + MRWR	I/II	Deely (30%)	Daracem 65 (3.0)
17	C Ash + Naph	I/II	Deely (30%)	Daracem 19 (10.0)
18	C Ash + Poly	I/II	Deely (30%)	ADVA Flow (3.0)

TABLE 5.2 Testing Matrix for Isothermal Calorimetry Mixtures (Continued)

Mix Number	Mix Description	Cement Type	SCM Type (% replacement)	Chemical Admixture (fl.oz per 100 weight cement)
19	C Ash + WR	I/II	Parish (30%)	Pozzolith 200N (4.0)
20	C Ash + MRWR	I/II	Parish (30%)	Daracem 65 (3.0)
21	C Ash + Naph	I/II	Parish (30%)	Daracem 19 (10.0)
22	C Ash + Poly	I/II	Parish (30%)	ADVA Flow (3.0)
23	F Ash + WR	I/II	Big Brown (20%)	Pozzolith 200N (4.0)
24	F Ash + MRWR	I/II	Big Brown (20%)	Daracem 65 (3.0)
25	F Ash + Naph	I/II	Big Brown (20%)	Daracem 19 (10.0)
26	F Ash + Poly	I/II	Big Brown (20%)	ADVA Flow (3.0)
27	F Ash + WR	I/II	Martin Lake (20%)	Pozzolith 200N (4.0)
28	F Ash + MRWR	I/II	Martin Lake (20%)	Daracem 65 (3.0)
29	F Ash + Naph	I/II	Martin Lake (20%)	Daracem 19 (10.0)
30	F Ash + Poly	I/II	Martin Lake (20%)	ADVA Flow (3.0)
31		III	x	x
32	F Ash + Naph + Retarder	III	Big Brown (20%)	Daracem 19 (10.0) / Daratard 17 (3.0)
33	F Ash + Poly + Retarder	III	Big Brown (20%)	Advaflow (3.0) / Daratard 17 (3.0)
34	F Ash + Naph + Retarder	III	Martin Lake (20%)	Daracem 19 (10.0) / Daratard 17 (3.0)
35	F Ash + Poly + Retarder	III	Martin Lake (20%)	Advaflow (3.0) / Daratard 17 (3.0)
36	F Ash + Naph + MRWR + Retarder	III	Big Brown (20%)	Daracem 19 (10.0) / Daracem 65 (3.0) / Daratard 17 (3.0)
37	F Ash + Naph + MRWR + Retarder	III	Martin Lake (20%)	Daracem 19 (10.0) / Daracem 65 (3.0) / Daratard 17 (3.0)

TABLE 5.3 Oxide Analysis for Type I/II Cement

Name	Chemical Formula	Weight (%)
Silicon Dioxide	SiO_2	20.38
Aluminum Oxide	Al_2O_3	4.27
Iron Oxide	Fe_2O_3	3.02
Calcium Oxide	CaO	64.21
Magnesium Oxide	MgO	1.14
Sodium Oxide	Na_2O	0.12
Potassium Oxide	K_2O	0.37
Titanium Dioxide	TiO_2	0.17
Manganic Oxide	Mn_2O_3	0.32
Phosphorous Pentoxide	P_2O_5	0.05
Zinc Oxide	ZnO	0.00
Chromium Oxide	Cr_2O_3	0.09
Sulfur Trioxide	SO_3	2.89
Loss on Ignition		2.63

Tricalcium Silicate	C_3S	59.20
Tricalcium Aluminate	C_3A	6.22
Dicalcium Silicate	C_2S	13.78
Tetracalcium Aluminoferrite	C_4AF	9.18

5.3.2 Results of Isothermal Calorimetry Data

Preliminary results from isothermal calorimetry testing showed that cooling concrete with LN did affect the hydration process of cement samples. Surprisingly, in all 37 mixtures, the LN-cooled mixtures had accelerated rates of heat evolution. The results in Figure 5.5 are typical results that were obtained from isothermal calorimetry testing (the unit "g" in the figure refers to weight of cement and not the weight of the paste). Results from other mixtures are shown in Appendix D. It shows that mixing groups B-C have a much shorter dormant period and a steeper slope during the acceleratory period, corresponding to a faster rate of reaction. In addition, the peak heat evolution for mixing group D is considerably higher than the other 3 mixtures. Most likely, the increased peak

height is a result of curing for 1 hour at 100°F before being cooled with LN. Therefore, additional cooling procedures were tested to isolate the effects of cooling time from the effects of the LN method.

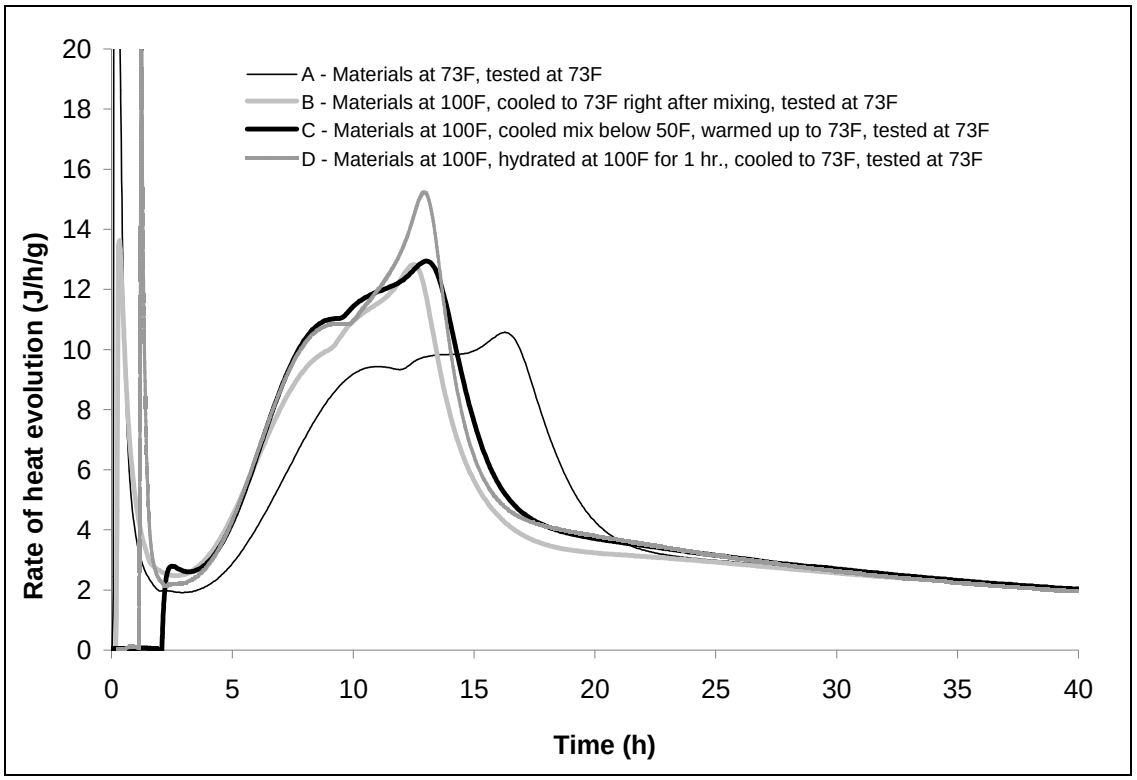


FIGURE 5.5 Heat evolution curves for isothermal calorimetry Mixture 4, A-D (C ash)

The following is a list of the additional cooling profiles (E-F) that were added to clarify the results of the initial testing:

E. Materials stored at 100°F, mixed hot materials and cooled to 73°F with liquid nitrogen the instant that cementitious materials and water made contact.
F. Materials stored at 100°F, mixed hot materials and cooled with chilled water (the water-to-cement ratio was kept constant by replacing the water with an equal amount of chilled water).

G. Materials stored at 100°F, mixed hot materials and cooled with ice (the water-cement ratio was kept constant by replacing 50% of the water with an equal amount of ice by weight).

These particular cooling procedures were chosen since they would be able to isolate the effect of cooling time from cooling method. Mixture E was chosen since the results of mixture B showed that hydration of cement paste at accelerated temperatures, even for 1 minute, caused a significant shift in the heat evolution curve. By performing mixture E, we would be able to determine if the preheating was causing the peak shift or, perhaps, some interaction between the cement hydration process and the LN. Mixture F and G were chosen for testing to determine the effects of traditional cooling methods on heat evolution. Figure 5.6 shows the calorimetry data for the control mixture along with the calorimetry data for the new cooling procedures, E-G.

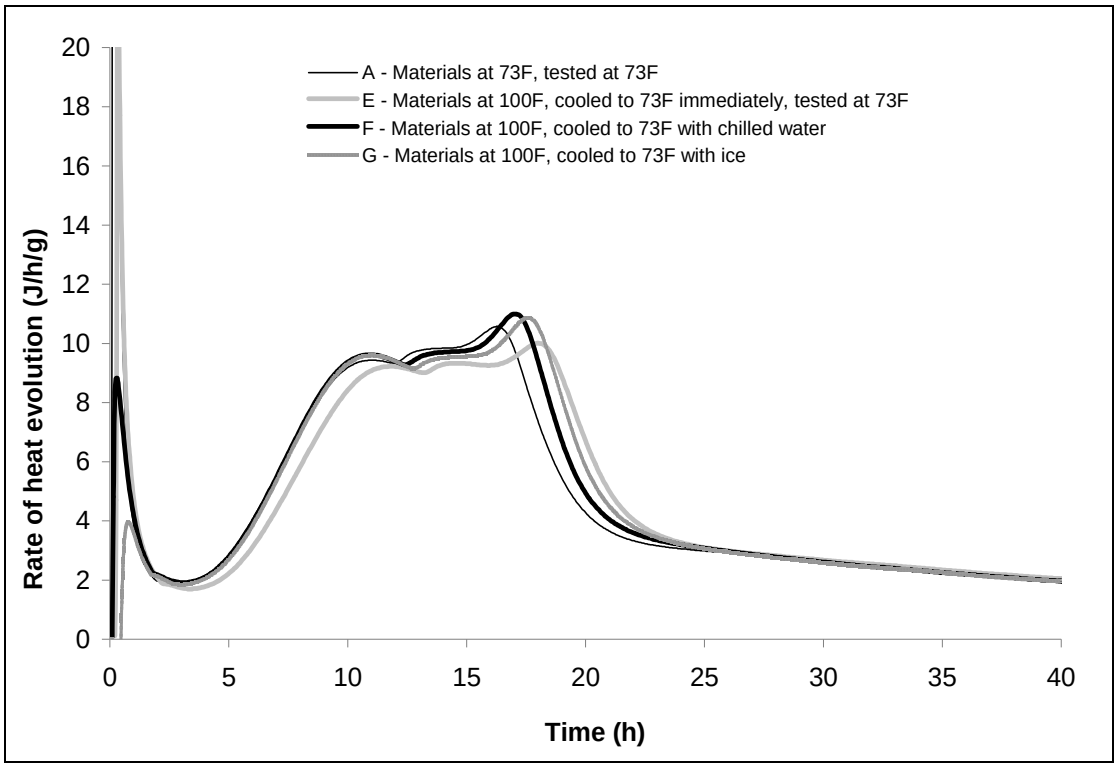


FIGURE 5.6 Heat evolution curves for isothermal calorimetry Mixture 4, A and E-G (C ash)

The data in Figure 5.6 shed light on the cause of the accelerated hydration occurring in methods B-D. The chilled water and ice mixtures (F and G) experience almost identical rates of heat evolution throughout the entire hydration process as the control mixture. Likewise, the mixture that is cooled immediately with LN (E) also follows the same calorimetry curve as the control mixture.

It appears that the accelerated rates of heat evolution were caused by the preheating of mixing materials. When the mixtures were cooled instantaneously on mixing, hydration followed the same path as the control mixture. This was independent of the cooling method. When cooling occurred 30 seconds to an hour after initial mixing, hydration was accelerated. This "delayed" cooling can only be achieved using LN; ice and chilled water always cool the mixture immediately upon contact of the cement and water. In the LN mixtures, the high temperatures (100°F) during this early period of "pre-heating" allows rapid dissolution of the cement grains and immediate formation of initial hydration products that accelerate the rest of the cement hydration process. If cooling with LN is not performed immediately, then the initial hydration process will be accelerated and cannot be reversed by cooling.

The implications of these results are significant since the delayed dosing of LN is what actually occurs at ready-mix plants. After mixing trucks are charged with their load of concrete, the concrete is mixed for a period of 3 to 15 minutes while the driver pulls away from the central mixer, picks up his batch ticket, and then waits in line for LN dosing. During this time, the concrete is allowed to hydrate at accelerated temperatures and will experience heat evolution similar to mixtures B and D, depending on how long it takes for the mixer to be cooled. However, it is unclear what the implications of this pre-heating and accelerated hydration are on the concrete properties. Concrete tested in the lab or field is not in an isothermal condition, so the results do not directly correlate. Nonetheless, slump is clearly influenced by pre-heating (section 3.3.4.3), which could be related to the isothermal calorimetry results showing increased early hydration on even slightly delayed dosing. In contrast, setting time does not appear to be affected (section 3.3.5.2). Perhaps the effects of pre-heating under non-isothermal conditions are limited to the very early hydration process, affecting slump. Setting may not be affected since it is more dependent on the later stages of hydration that are influenced more by the

concrete's actual temperature at the time of setting than by pre-heating.

5.4 X-RAY DIFFRACTION (XRD)

X-ray powder diffraction is a powerful tool for studying crystalline materials. Cement phases and some cement hydration products are crystalline and possess unique x-ray diffraction patterns. For powder diffraction, only x-rays with short wavelengths are used to penetrate deep into materials and extract information about the atomic structure (Ichimura and Manning, 2004).

As x-rays pass through different types of matter, the radiation interacts with orbital electrons in atoms resulting in scattering of the x-rays (Ichimura and Manning, 2004; Schields, 2004; Blackwood et al., 2001). Atoms that are organized into a regular, repeating structure make a crystalline material. Most crystals consist of many sets of planes of atoms that have a specific interplanar distance between them, which results in x-rays that are emitted at characteristic angles based on the spaces between the atomic planes. The relationship between wavelength, atomic spacing (d), and angle is expressed as Bragg's law (Scrivener et al., 2004; Blackwood et al., 2001):

$$n\lambda = 2d\sin\theta \qquad \text{Equation 5-4}$$

where n is an integer, λ is the wavelength of the x-ray radiation, d is the spacing of the crystal planes, and θ is the angle of the diffraction peak. Peak intensities are determined by the orientation and types of atoms in a crystal structure. In addition, the peak shape can also be affected by equipment parameters (Scrivener et al., 2004).

X-ray diffractometry is an attractive analytical technique for concrete research because of the speed and simplicity at which testing is conducted. In addition, the technique is nondestructive and requires only a few grams of material for analysis. Some of the x-ray diffractometers (Figure 5.7) are automated and contain an auto-sampler, allowing multiple samples to be analyzed over days or even weeks without any interaction from the operator.

FIGURE 5.7 X-ray diffractometer

5.4.1 Experimental Methods for X-ray Diffraction

Cement phases and hydration products are generally crystalline and can be analyzed by x-ray diffraction. Cement paste samples from 16 different mixtures were analyzed to characterize their hydration products. The different mixtures were cement pastes without any SCMs that were subjected to varying degrees and durations of LN dosing to determine the effects that LN would have on the development of hydration products. Samples from each mixture were taken at 30 minute intervals over a 4 hour period so that hydration curves could be generated that would show the amount of hydration products that had developed over time. Table 5.4 shows the mixing matrix for x-ray diffraction testing and presents the starting and ending temperatures and details about cooling for each mixture. An oxide analysis for the cement is shown in Table 5.3.

TABLE 5.4 Details about X-ray Diffraction Mixtures

Mix Name	Starting Temp (°F)	Ending Temp (°F)	Time of cooling
C73	73.5	73.5	No cooling
C100	100.0	100.0	No cooling
LN73-00	100.0	73.5	Cooled immediately during mixing
LN73-15	100.0	74.6	Cooled 15 minutes after mixing
LN73-45	100.0	71.3	Cooled 45 minutes after mixing
LN73-75	100.0	74.4	Cooled 75 minutes after mixing
LN73-105	100.0	73.3	Cooled 105 minutes after mixing
LN73-135	100.0	78.6	Cooled 135 minutes after mixing
LN50-00	100.0	47.6	Cooled immediately during mixing
LN50-15	100.0	49.0	Cooled 15 minutes after mixing
LN50-45	100.0	49.1	Cooled 45 minutes after mixing
LN50-75	100.0	47.9	Cooled 75 minutes after mixing
LN32-00	100.0	33.2	Cooled immediately during mixing
LN32-15	100.0	33.8	Cooled 15 minutes after mixing
LN32-45	100.0	33.4	Cooled 45 minutes after mixing
LN32-75	100.0	32.5	Cooled 75 minutes after mixing

Cement paste samples were prepared for analysis over a 2 day period. Cement paste was sampled from individual mixtures at 30 minute intervals over a 4 hour period and placed under vacuum with a Buchner filter and filtering flask, as shown in Figure 5.8. The filtering flask captured pore solution that was extracted from the wet paste and the Buchner filter retained the desiccated paste sample. After vacuuming, the desiccated paste samples were soaked for at least 24 hours in ethanol and then wet ground with ethanol in a mortar and with a pestle. Rutile, an internal standard for quantitative XRD analysis, was mixed 10% by weight with the cement sample. Once the ethanol had completely evaporated, the powder was placed in a sample holder and analyzed in the x-ray diffractometer. The program DIFFRACplus was used to perform quantitative analysis of the phases from the XRD scans using the Rietveld method (Scrivener et al., 2004). The pore solution that was captured in the filtering flask was placed in plastic containers and stored in a refrigerator set to 40°F to preserve the solutions.

FIGURE 5.8 Pore solution extraction from early-age cement pastes

Cement pastes were mechanically mixed in accordance with ASTM C 305, "Standard Practice for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency." All of the mixtures contained 1300 grams of TXI Type I/II cement, and had a water-cement ratio of 0.44. Subsequent LN applications occurred at prescribed times, as shown in the mixing matrix in Table 5.4.

The tests presented in this section compare quantities of ettringite, calcium hydroxide, and monosulfoaluminate from LN mixtures to two control mixtures. The first control mixture, C73, is a cement paste sample where all mixing materials were stored at 73°F, mixed at 73°F, and allowed to hydrate at 73°F. C stands for controlled samples that were uncooled by LN. LN is for liquid nitrogen cooled samples. The first number is the fresh temperature or temperature after cooling, and the second number is the time of cooling. The second control mixture, C100, is a cement paste sample where all mixing

materials were stored at 100°F, mixed at 100°F, and allowed to hydrate at 100°F. The remaining mixtures in Table 5.4 are all cement pastes that were cooled with LN to different temperatures (32°F, 50°F, and 73°F) at various times (0, 15, 45, 75, 105, and 135 minutes). The hydration products in the LN mixtures are compared to the hydration products in both C73 and C100.

5.4.2 Results of XRD Analysis

The results presented in this section compare data from five representative mixtures from the testing matrix. The mixtures are C73, C100, LN73-00, LN50-00, and LN32-00. None of the delayed dosing mixtures are presented in this section since the results are generally the same as the LN mixtures that were cooled immediately to their respective temperatures. XRD results for delayed dosing mixtures can be found in Appendix E.

Results in Figure 5.9 show ettringite quantities for five different cement pastes. A trendline is included in the figure as a baseline average since most of the data were measured within the operational noise level of the instrument and below the resolution of the analysis technique. The trendline shows that the LN mixtures developed the same quantities of ettringite as did the control mixtures. Therefore, XRD results suggest that LN dosing does not affect the early formation of ettringite in cement paste.

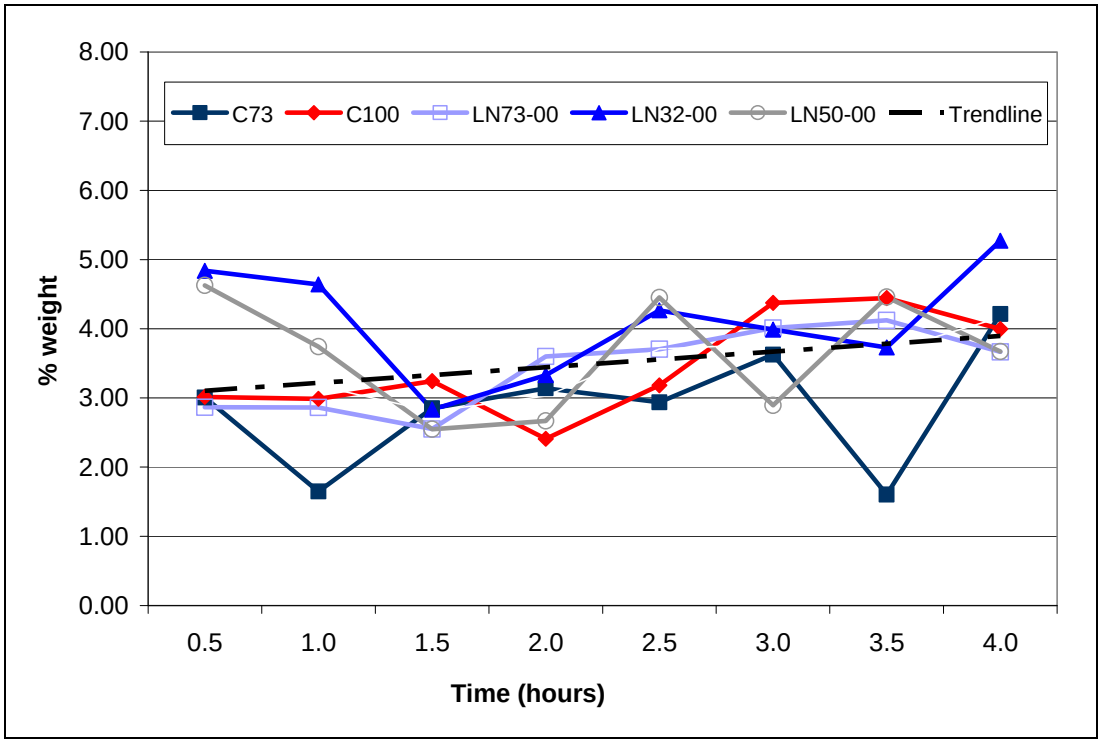


FIGURE 5.9 Ettringite analyses by x-ray diffraction for five LN-cooled cement mixtures

Results of XRD testing for calcium hydroxide content (CH) are shown in Figure 5.10. The rate of CH development is faster in mixture C100. This result is not unexpected since the mixing materials for this mixture were preheated and then allowed to hydrate at 100°F. Therefore, the increased rate of CH development is a result of the increase reaction rate of C_3S due to the increased temperature. The LN-cooled mixtures appear to develop CH at the same rate as the control mixture, C73. In other words, preheated cement mixing materials that are cooled with LN during mixing do not show an increased rate of CH development when compared to the control hydrated at 73°F. Therefore, XRD results suggest that LN has no effect on the early formation of calcium hydroxide in cement paste.

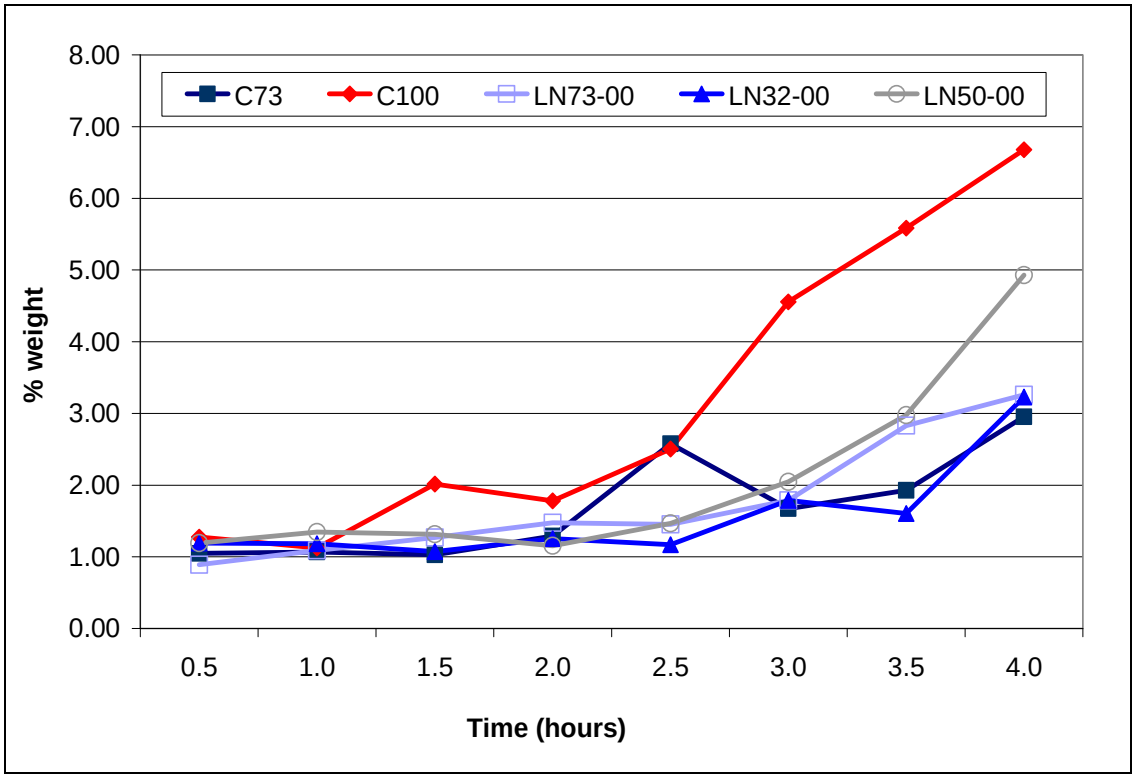


FIGURE 5.10 Calcium hydroxide analyses by x-ray diffraction for five LN-cooled cement mixtures

Results of monosulfoaluminate (AFm) content are shown in Figure 5.11. There appears to be an increased rate of monosulfoaluminate (AFm) development in mixture C100. This result is not unexpected since the mixing materials for this mixture were preheated and then allowed to hydrate at 100°F. The LN cooled mixtures appear to develop AFm at the same rate as the control mixture, C73. However, it should be noted that the quantity of AFm measured is within the error of the Rietveld technique for quantitative analysis of 2-3%. Therefore, few valuable conclusions can be drawn from these data. It can be assumed that that LN has no effect on the early formation of AFm in cement paste.

XRD analyses for ettringite, calcium hydroxide, and monosulfoaluminate show that LN mixtures developed the same quantities of hydration products as control mixtures. Therefore, LN dosing does not appear to affect the formation of ettringite,

calcium hydroxide, or monosulfoaluminate in cement paste mixtures. More testing was conducted to confirm the results that were obtained through XRD testing. Solution analyses were performed to monitor the concentration of specific elements in the pore solution that are required in the formation of ettringite, calcium hydroxide, and monosulfoaluminate, such as calcium and sulfur. In addition, ESEM imaging was used to examine the formation hydration products.

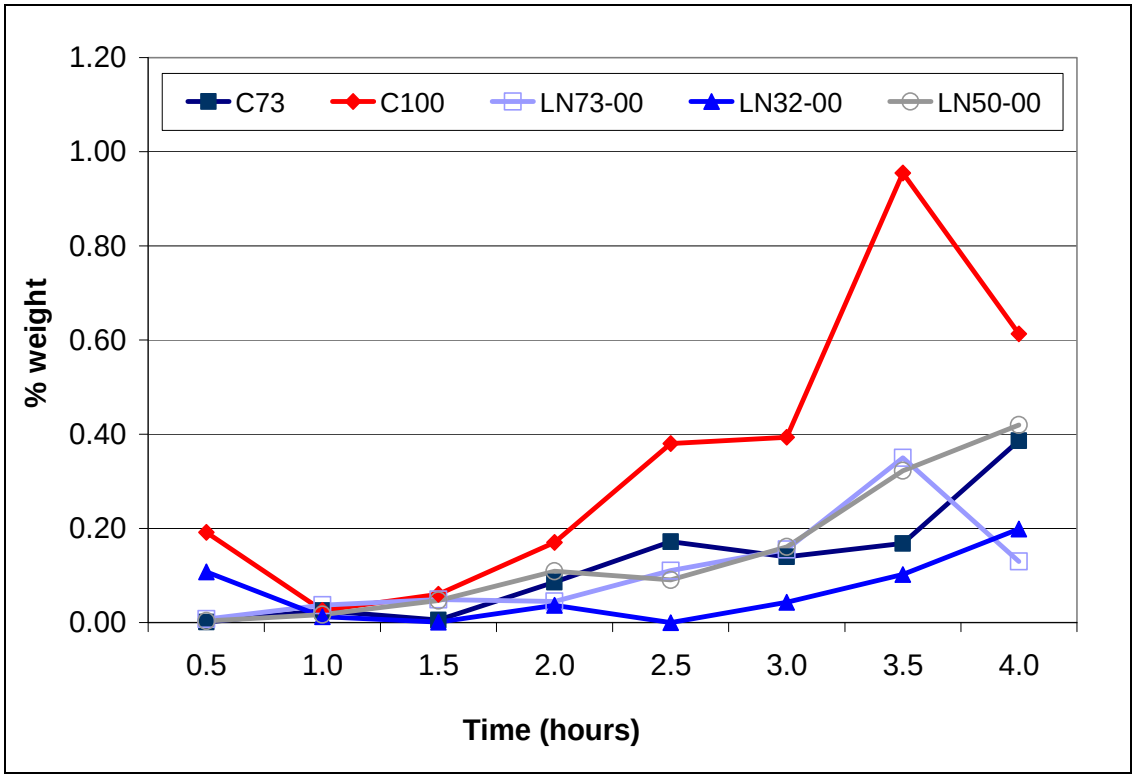


FIGURE 5.11 Monosulfoaluminate analysis by x-ray diffraction for five LN-cooled cement mixtures

5.5 INDUCTIVELY COUPLED PLASMA (ICP)

Inductively coupled plasma (ICP) is an extremely useful technique for analyzing ion concentrations in solutions. For concrete research, ICP can be used to analyze pore solutions extracted from early age cement samples or from hardened concrete. The concentration of ions in pore solution samples is important in concrete research in that it

is linked directly to the hydration process of cement. As cement starts to dissolve in water, ions from the cement grain diffuse into the surrounding water. The concentrations of individual ions in solution continue to increase as the cement dissolves until they are consumed by hydration product formation. Ion concentrations fluctuate widely during the hydration process since many ions dissolve into the pore solution within the first few minutes of hydration and are slowly consumed throughout the remainder of the process. By monitoring the concentration of individual ions, it is possible to determine the time at which certain hydration products are forming.

ICP has a high temperature (7000° - 8000° K) excitation source that uses argon plasma that effectively excites and ionizes atoms (Boss and Freeden, 1997). The excited atoms emit radiation at a wavelength that is characteristic of that particular element (Boss and Freeden, 1997). The intensity of emitted radiation is proportional to the concentration of atoms or ions present in the solution (Boss and Freeden, 1997). This technique is also often referred to as ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry) since it uses spectral analysis to identify elements. One of the main benefits of ICP-OES is that it can analyze many of the elements on the periodic table and can perform the analysis simultaneously.

5.5.1 Experimental Methods for ICP

Solution samples from 8 mixtures in Table 5.4 were analyzed for ion concentrations. Due to cost considerations, mixtures were selected that would allow for a complete analysis without having to analyze all of the samples. The different mixtures were subjected to varying degrees and durations of LN dosing to determine the effects that LN would have on the development of hydration products. The mixtures that were analyzed with ICP are C73, C100, LN73-00, LN73-15, LN73-45, LN73-75, LN32-00, and LN32-15. Mixing and sample preparation procedures are outlined in section 5.4.1. An oxide analysis for the cement is shown in Table 5.3.

Cement paste pore solution samples were analyzed for calcium (Ca), sulfur (S), sodium (Na), aluminum (Al), silicon (Si), and potassium (K). However, due to some calibration inaccuracies, only the data from Ca, S, and K can be used. The tests presented

in this section compare concentrations of Ca, S, and K from LN mixtures to the control mixtures, C73 and C100. Details about each mixture are shown in Table 5.4.

5.5.2 Results of ICP Analysis

The results presented in this section compare data from six representative mixtures from the testing matrix. The mixtures tested are C73, C100, LN73-00, LN73-75, LN32-00, and LN32-15. The delayed dosing mixtures, LN73-15 and LN73-45, are not presented in this section since the results can be interpolated between LN73-00 and LN73-75. ICP results for LN73-15 and LN73-45 can be found in Appendix F.

Data for calcium concentration over the first four hours of hydration are presented in Figure 5.12. Mixture C100 appears to have a constant concentration of calcium until 3 hours after mixing, when the calcium concentration drops. The calcium concentrations of the LN mixtures appear to remain constant throughout the 4 hour testing period without any reduction in concentration. The behavior of mixture C73 is unexpected. It appears that the calcium concentration decreases at 3.5 hours, only to increase again at 4 hours. The more likely scenario is that the point at 3.5 hours is in error, and that the concentration of calcium ions in this sample is constant.

Calcium is an important ion in the formation of hydration products. The majority of cement hydration products contain calcium, including, most notably, calcium hydroxide (CH) and calcium silicate hydrate (C-S-H). Therefore, a reduction in the concentration of calcium in solution suggests that CH and/or C-S-H is forming. The data in Figure 5.12 suggest that CH begins forming in the high temperature C100 sample at 3 hours. The data also suggest that no CH is forming in the room temperature control, C73, or in the LN dosed mixtures. This result is consistent with the XRD data from Figure 5.10 which show that the formation of calcium hydroxide is not affected by LN dosing.

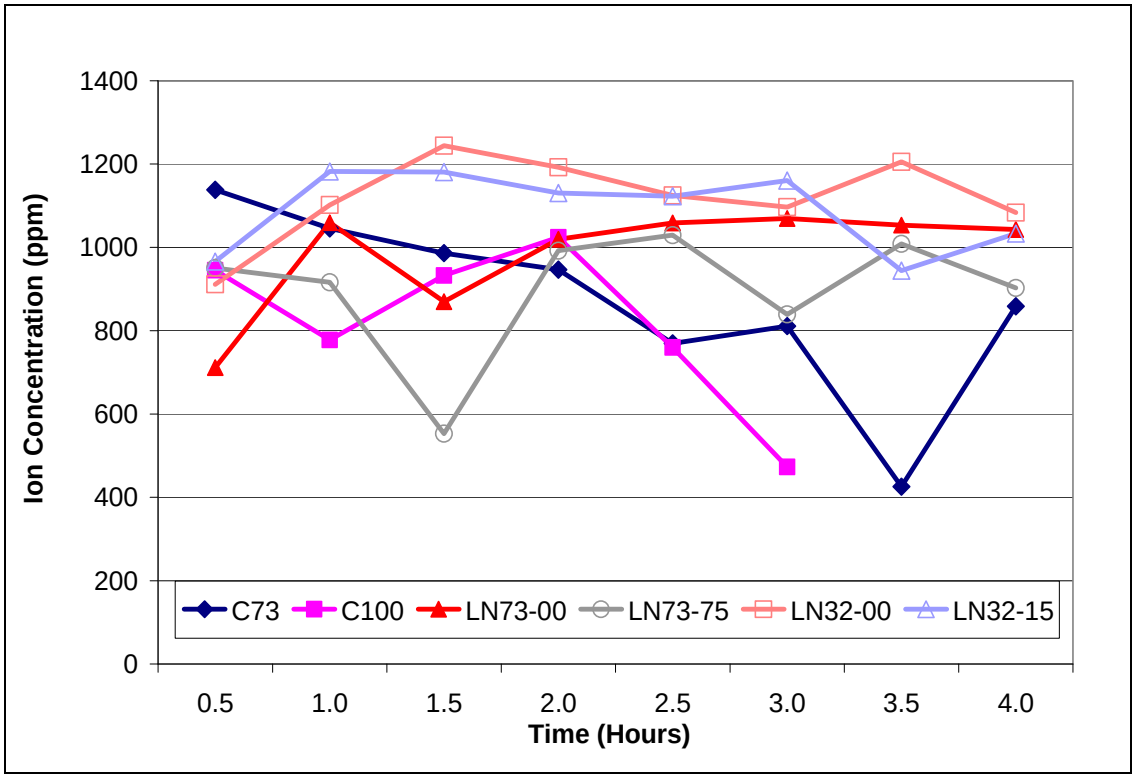


FIGURE 5.12 Calcium concentrations for six different cement paste mixtures

Results from the testing of sulfur concentration are shown in Figure 5.13. The sulfur concentration is higher in mixture C100 and increases after 2 hours. Since this mixture was allowed to hydrate at 100°F, more ions are solubilized. Mixture LN73-75 initially behaves in the same manner as C100 since both mixtures are hydrating at 100°F during the same period of time. However, the behavior of mixture LN73-75 changes after it is cooled with LN at 75 minutes and begins to solubilize ions similar to the control and LN mixtures. The control and LN mixtures have a relatively constant initial sulfur concentration, which then starts to increase slightly after about 3 hours.

Gypsum and other calcium sulfate compounds in cement dissolve upon contact with water, causing high initial concentrations of sulfate ions in solution. The sulfate ions react with calcium aluminate in the cement to form ettringite within the first few hours after mixing with water. Therefore, any differences in the rate at which sulfur is consumed in the LN mixtures would indicate that LN may be affecting the formation of

ettringite. The data in Figure 5.13 indicate that the formation of ettringite in LN mixtures is similar to the C73 control mixture. This suggests that LN does not affect the formation of ettringite crystals. These results are consistent with the XRD data in Figure 5.9.

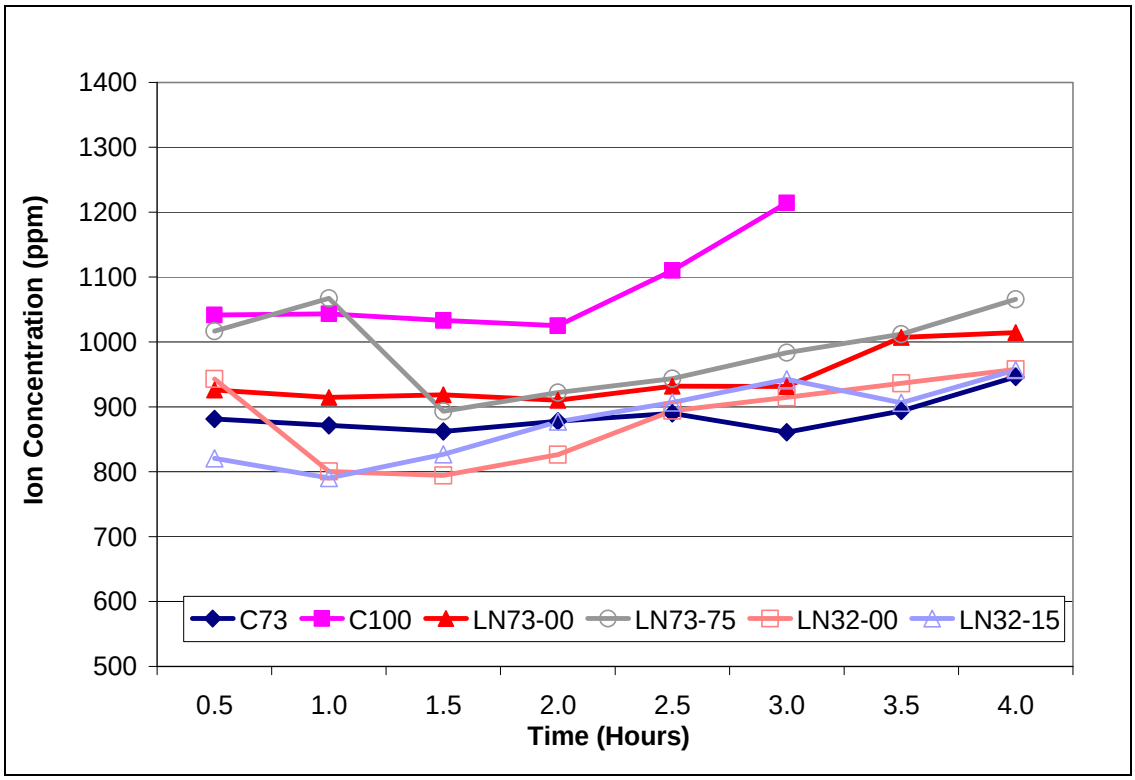


FIGURE 5.13 Sulfur concentrations for six different cement paste mixtures

Potassium concentration results are shown in Figure 5.14. Potassium was analyzed by the ICP since alkalis help to maintain the high pH of cement pore solution. In all samples, the potassium concentration increases with time, but the rate is faster in mixture C100 than in the other mixtures. Again, the rapid increase in the potassium ion concentration for mixture C100 can be attributed to increased temperature; the solubility of potassium is increased with temperature. The behavior of the LN mixtures is similar to the control mixture indicating that LN dosing has no effect on the solubility of potassium.

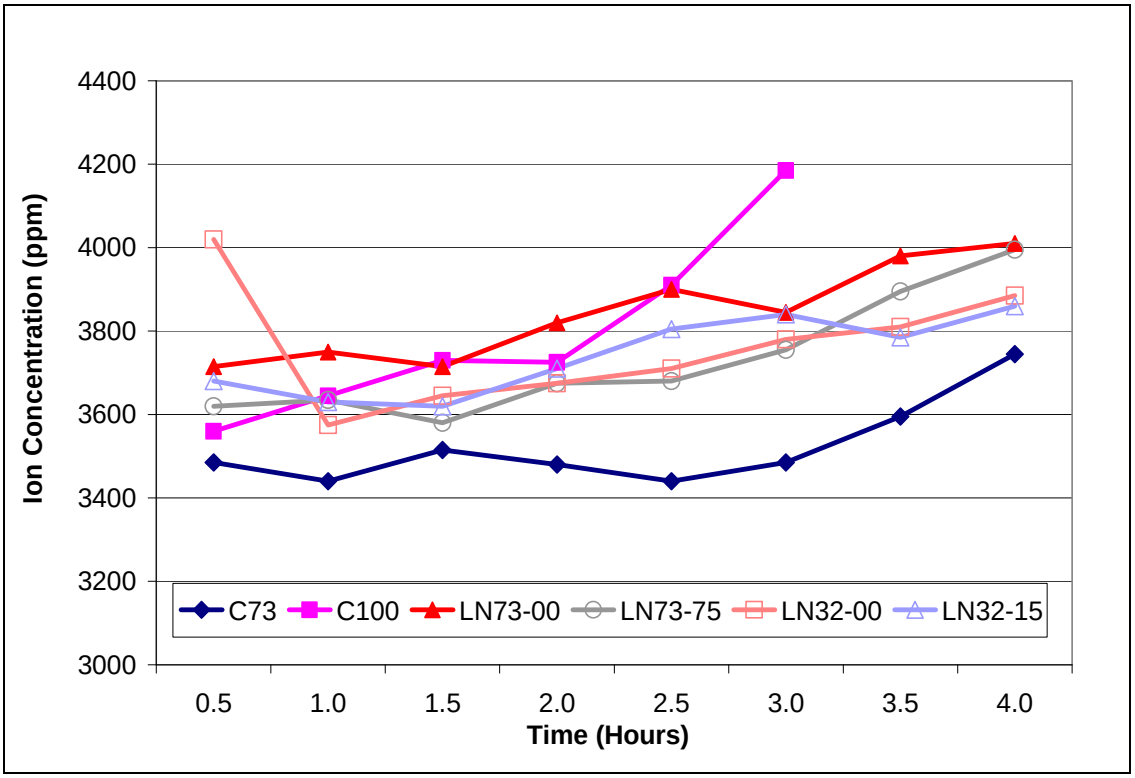


FIGURE 5.14 Potassium concentrations for six different cement paste mixtures

5.6 ENVIRONMENTAL SCANNING ELECTRON MICROSCOPY (ESEM)

The environmental scanning electron microscope (ESEM) has revolutionized research of cement-based materials. Since water is a central part of the microstructure of cement paste and concrete, techniques are needed that allow for the study of wet samples. Often, cement and concrete research incorporates the use of the scanning electron microscope (SEM) to perform image analyses of cement-based materials. However, the high-vacuum environment in the SEM chamber makes it impossible to image wet samples without first drying them. As well, the elaborate specimen preparation techniques for SEM damaged the microstructure of cement-based specimens. With the ESEM (Figure 5.15), cement samples can be analyzed in a wet environment without any damage caused from drying or from specimen preparation (Neubauer and Jennings, 1996). Although the results from the ESEM only provide qualitative data regarding

cement hydration products, the results are being used in this study to confirm the results of quantitative techniques such as XRD and ICP.

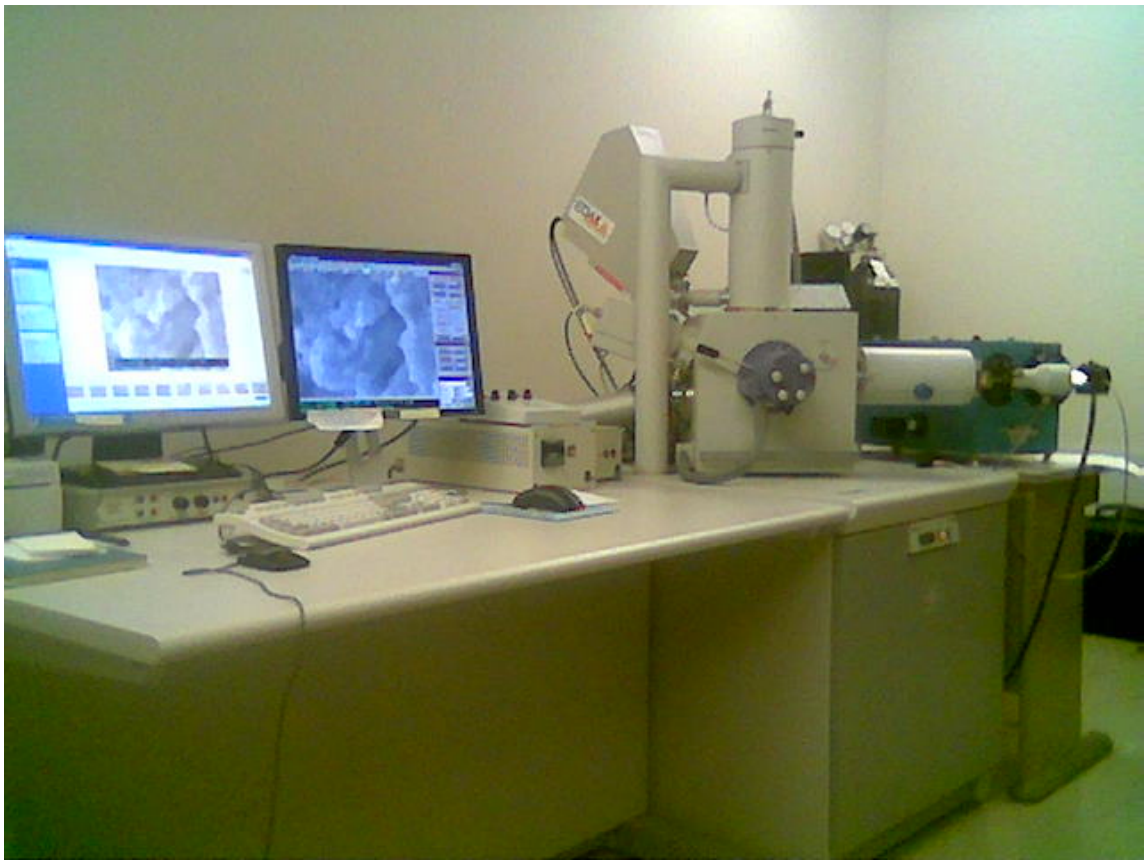


FIGURE 5.15 Environmental Scanning Electron Microscope

The specimen chamber of an ESEM can be operated with a poor vacuum up to 10 Torr of vapor pressure. To achieve "wet mode" imaging, the specimen chamber has to be isolated from the rest of the vacuum system by valves, pressure-limiting apertures, and a large-diameter bypass tube (Robinson, 2003). Although the ESEM can accommodate different gases in the specimen chamber, the most common imaging gas is water vapor. A separate vacuum pump for the specimen chamber allows for fine control of the vapor pressure in the chamber, which can be maintained as high as 100% relative humidity for hydrating cement samples. The electron beam produces primary electrons which are accelerated toward the cement sample causing a collision that ejects secondary electrons

from the surface of the sample. The secondary electrons are scattered and collide with water molecules in the specimen chamber. The water molecules act as a cascade amplifier by delivering the secondary electron signal to the positively charged gaseous secondary electron detector (Robinson, 2003). Due to collisions with secondary electrons, water molecules are now positively charged and are attracted to the cement sample, serving to neutralize the effects of charging (Robinson, 2003). This is the reason why samples do not require a conductive coating within the ESEM.

5.6.1 Experimental Methods for ESEM

Initial imaging of cement samples was conducted on three different hydrating cement pastes, C73, LN73-00, and LN50-00. An oxide analysis for the cement is shown in Table 5.3. The conditions of these samples are described in Table 5.4. ESEM images for these samples showed very few hydration products during the first 4 hours of hydration. These images can be found in Appendix G. It was then decided to examine fracture surfaces of hardened and dried pastes rather than using fresh pastes. This method does not take true advantage of the ability of the ESEM to monitor hydration in situ, but still takes advantage of the reduced sample preparation time.

Five additional mixtures, C73, LN73-00, LN73-105, LN50-00, and LN32-00, were made and sampled at 1, 4, and 24 hours. These particular mixtures were imaged by ESEM to provide a general range of mixtures that would allow for a complete analysis without having to analyze a full spectrum of mixtures. The cement paste samples were soaked in ethanol for 24 hours to stop hydration and then dried in a desiccator. The fractured surfaces were removed from the desiccator, mounted on aluminum posts, and placed in the ESEM for analysis. At this point, the high vapor environment in the ESEM was no longer needed to keep the samples hydrated. However, low vapor pressure was still required in the sample chamber to provide conductivity since the specimens were not carbon coated.

Images at magnifications of 5000X from fractured surfaces revealed cement hydration products. Although the ESEM can image at higher magnifications, image resolution was impaired by the water vapor in the chamber. All of the images presented

here were taken after 24 hours of hydration. The other images taken at 1 and 4 hours showed relatively little in terms of hydration products. These images are also shown in Appendix G. Mixing and specimen preparation procedures are outlined in section 5.4.1.

5.6.2 Results of ESEM Analysis

Figures 5.16 to 5.20 are ESEM images of fractured cement paste surfaces after 24 hours of hydration. Although the results from the ESEM only provide qualitative data regarding the formation of cement hydration products, the images are used to confirm the similarity of formation and morphology of hydration products in LN-cooled samples compared to control samples.

The images all show the presence of ettringite crystals growing in the paste as well as a thin layer of C-S-H covering cement grains. Because of the resolution limitations of the instrument, it was very difficult to image CH and AFm. Although these hydration products do not appear in the following images, it does not disprove their existence in these samples. Based on the images presented in Figures 5.16 to 5.20, it appears that dosing cement samples with LN is not affecting the growth of ettringite or C-S-H during cement hydration.

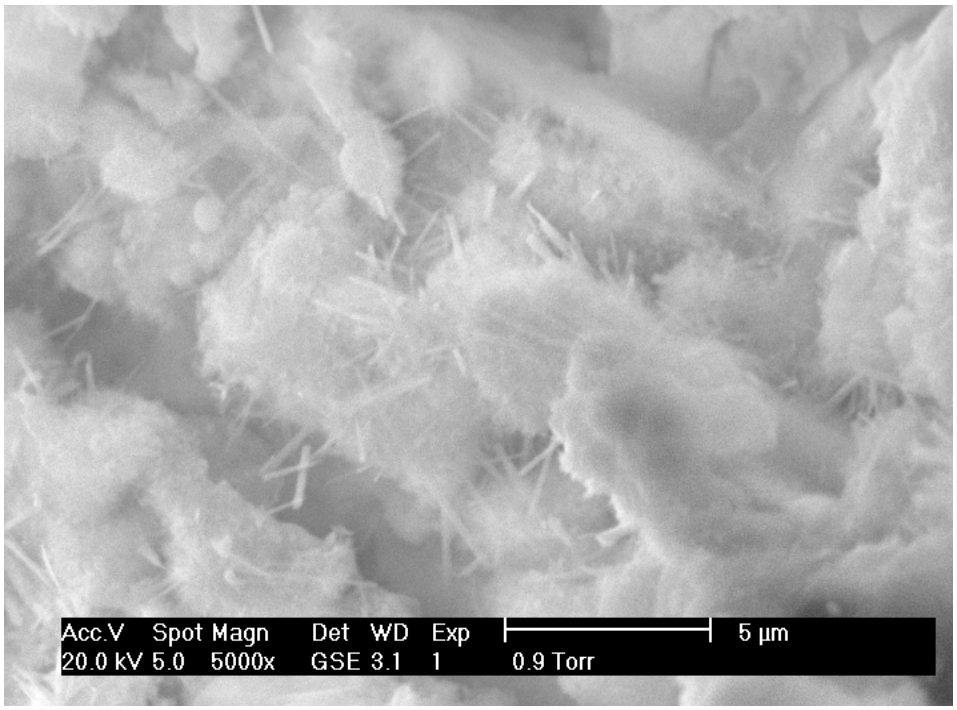


FIGURE 5.16 ESEM image of fractured cement paste surface from mixture C100 after 24 hours of hydration

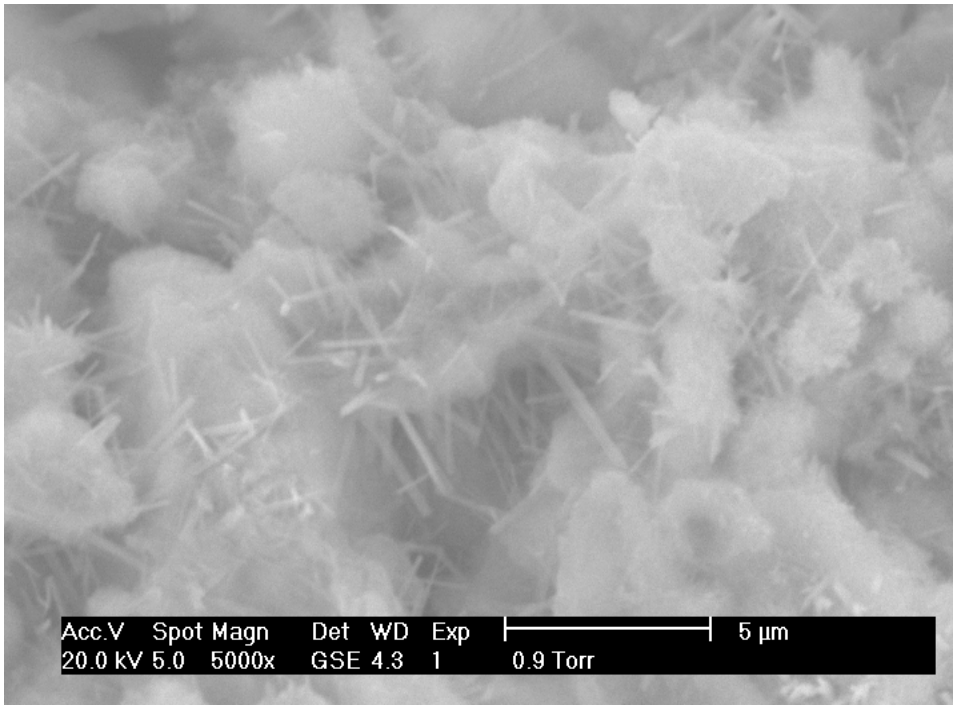


FIGURE 5.17 ESEM image of fractured cement paste surface from mixture LN73-00 after 24 hours of hydration

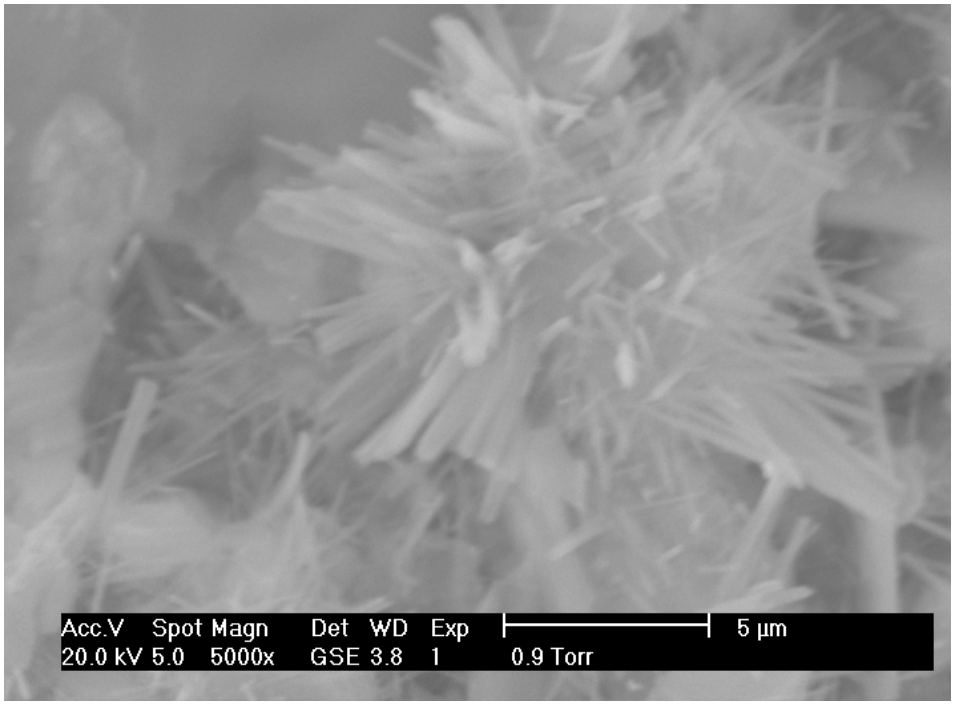


FIGURE 5.18 ESEM image of fractured cement paste surface from mixture LN73-105 after 24 hours of hydration

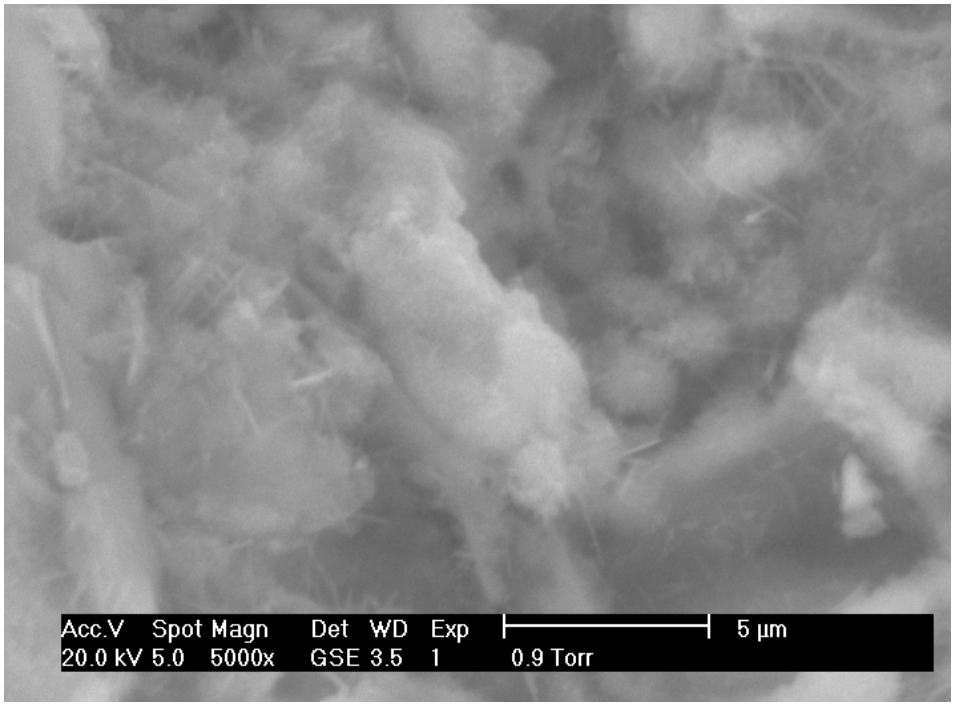


FIGURE 5.19 ESEM image of fractured cement paste surface from mixture LN50-00 after 24 hours of hydration

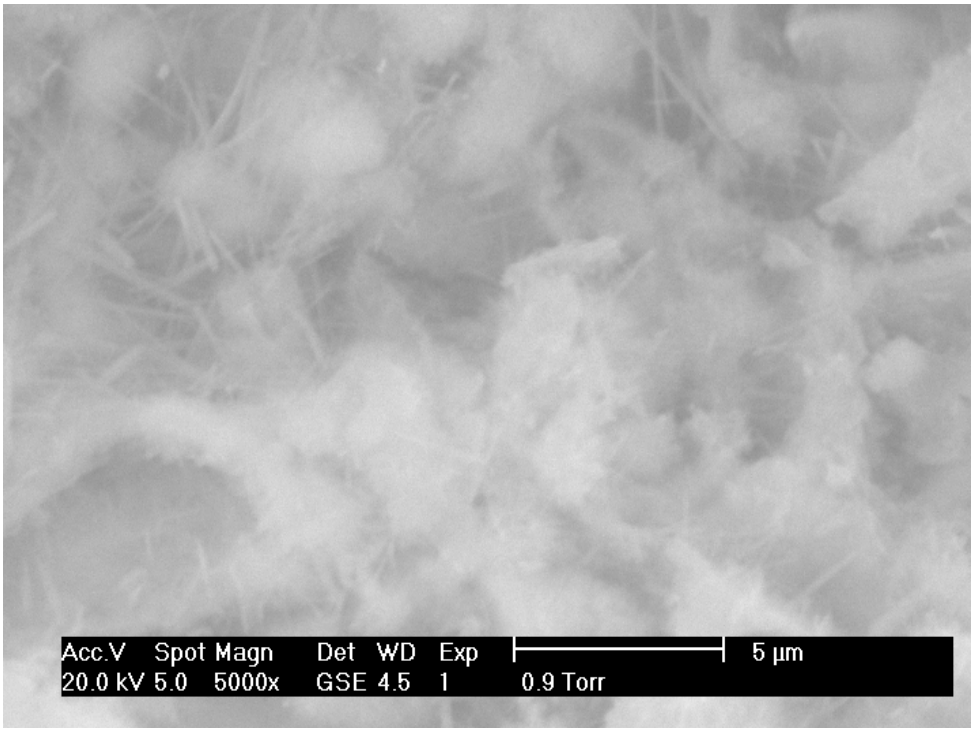


FIGURE 5.20 ESEM image of fractured cement paste surface from mixture LN32-00 after 24 hours of hydration

5.7 CONCLUSIONS

Semi-adiabatic calorimetry testing shows that LN has very little effect on the rate of hydration of concrete samples. Results show that only four out of 42 curve-fit parameters, α, τ, and β, compared between LN and control mixtures were considered statistically significant. None of the results that were considered statistically significant exceeded the precision threshold by more than 3.9% for α and 2.2% for β. In addition, no mixture had more than one curve fit parameter that was considered statistically significant. Therefore, it appears that LN dosing has relatively no effect on the rate of hydration of concrete mixtures.

Isothermal calorimetry data show that the use of LN to cool fresh cement paste does not affect the rate of heat evolution provided that cooling is simultaneous with mixing. Chilled water and ice mixtures experienced similar rates of heat evolution as the control mixtures, as did LN-cooled mixtures where the cooling was achieved immediately on mixing. In mixtures where LN dosing was performed as little as 30

seconds after mixing, test showed increased rates of heat evolution when compared to the control mixtures. The cause for the accelerated heat emission was due to preheating of mixture materials before LN application. If cooling with LN is not performed immediately, then the hydration process will be accelerated and cannot be reversed by subsequent cooling. This poses a problem for ready-mix concrete companies since LN dosing usually does not occur immediately in the central mixer but at a separate location at the plant. Typically this occurs within 5 to 15 minutes of charging the mixer which would make this a delayed dosing application. The consequences of this increased rate of reaction can be seen in decreased slumps discussed in Chapter 3. The pre-heating does not appear to affect setting time, Chapter 3. In order to further investigate this problem, extensive testing was conducted on concrete mixtures to determine the effects that delayed dosing would have on setting time and strength (compressive and splitting tensile). These results are found in Chapter 6.

An X-ray diffraction (XRD) analysis for ettringite, calcium hydroxide, and monosulfoaluminate shows that LN mixtures developed the same quantities of hydration products as control mixtures. Therefore, LN dosing does not appear to affect the formation of ettringite, calcium hydroxide, or monosulfoaluminate in cement paste mixtures.

Cement paste pore solutions were analyzed by inductively coupled plasma (ICP) for calcium, sulfur, and potassium. The dissolution and consumption of calcium, sulfate, and potassium ions in LN mixtures appear to be similar to the room temperature (73°F) control mixture. Therefore, LN dosing has no effect on these processes.

Although the results from the environmental scanning electron microscopy (ESEM) only provide qualitative data regarding the formation of cement hydration products, the images are used to examine the presence, morphology, and distribution of hydration products in LN cooled samples. The images all show the presence of ettringite crystals growing in the cement matrix as well as a thin layer of calcium silicate hydrate covering cement grains. Because of the resolution limitations of the instrument, it was very difficult to image calcium hydroxide and ettringite. Based on ESEM images of hydrated cement paste, it appears that dosing cement samples with LN is not affecting the growth of ettringite or calcium silicate hydrate during cement hydration.

CHAPTER 6: DELAYED DOSING OF CONCRETE MIXTURES

6.1 INTRODUCTION

The curing temperature of concrete is the factor that has the most influence on setting time. Higher curing temperatures result in faster reactions between cement and water, causing rapid setting in concrete. Increased rates of setting result in greater difficulty in placement, consolidation, and finishing. Slowing the rate of setting can be achieved by lowering the concrete temperature, either through the use of SCMs or possibly liquid nitrogen (LN). The research presented in this section compares the setting times of concrete mixtures cooled with LN at different times and to varying temperatures. It is of interest to concrete producers to be able to delay LN dosing, rather than dosing immediately. This would allow the flexibility to batch concrete at one location, transport it to another location, and then cool with LN. In addition, it is of interest to be able to use LN to make concrete very cold, thereby extending the travel time of ready-mix trucks to job sites without having their loads rejected. Furthermore, delaying setting of concrete at a job site by reducing the temperature would allow contractors to put trucks "on hold" during construction delays without losing batches or sacrificing performance.

For this reason, research was conducted to determine if the use of LN and the time at which dosing occurs affects the setting time and strength of concrete. Testing was conducted using isothermal calorimetry, setting time tests, and compressive and splitting tensile strength testing.

6.2. EFFECTS OF DELAYED DOSING ON SETTING TIME

The temperature at which cement hydrates controls the rate of reaction. Heat causes cement hydration to accelerate, causing faster setting and higher early strengths. Conversely, cold temperatures slow down cement hydration reactions, causing a delay in setting time and a reduction in early concrete strength.

Hot weather concreting poses several problems that must be addressed to ensure a successful concrete placement. The most important aspect in hot weather concreting is to

ensure that there is adequate time to transport, place, and finish the concrete before it sets. Typically, transport requires the most amount of time in the placement process. In addition, delays are ever-present in the construction industry and cause concrete to sit in trucks longer than is allowed by specifications. The concrete in these particular trucks is rejected and cannot be used on the project. However, LN technology offers an attractive solution that may prevent the refusal of fully-charged mixing trucks.

In the research presented in this dissertation up to this point, setting times were measured on concrete cooled with LN after several minutes of mixing. This new round of testing required that we delayed LN dosing for up to a couple of hours before performing setting time tests. These new tests would allow us to see if delaying the cooling of concrete with LN has any adverse affects on the setting time and strength of concrete as compared to concrete that is cooled after only a few minutes of mixing. This opens up the possibility of cooling concrete mixtures on-site to avoid rejecting truck loads of concrete simply because the concrete had been in the mixing truck for too long. With other cooling methods, delayed cooling was not possible since the cooling methods were part of the mixing water and required immediate application. The research presented in this chapter compares the setting times of concrete mixtures cooled with LN at different times and to varying temperatures.

6.2.1 Experimental Methods for Delayed Dosing Concrete Mixtures

The mixture design for these concrete mixtures was a six sack mixture consisting of TXI Type I/II cement, 30% Class F fly ash supplied by Headwaters Resources from the Limestone plant in Jewett, TX, coarse and fine aggregate as discussed in section 3.3.1, water-cement ratio of 0.44, and a water-reducing admixture (Grace WRDA 35, 6.50 fl. oz. per 100 weight cement). All mixing materials were heated to 100°F prior to mixing except for the control mixture (C73). Table 6.1 shows the mixing matrix for delayed dosing testing and presents the starting and ending temperatures and details about cooling for each mixture. Cooling times were measured from the moment water was added to the concrete mixture to when the mixture obtained the target temperature. It should be noted that LN-00 does not mean that the mixture was cooled immediately after

pouring water into the mixture. Rather, LN-00 was dosed approximately 5 minute after water was poured into the mixture to ensure that the mixture was properly agitated before cooling.

TABLE 6.1 Details about Delayed Dosing Mixtures

Mix Name	Starting Temp (°F)	Ending Temp (°F)	Time of cooling
C73	73.0	73.0	No cooling
C100	100.0	100.0	No cooling
LN73-00	100.0	71.1	Cooled immediately during mixing
LN73-15	100.0	73.4	Cooled 15 minutes after mixing
LN73-45	100.0	73.9	Cooled 45 minutes after mixing
LN73-60	100.0	74.8	Cooled 60 minutes after mixing
LN40-00	100.0	43.2	Cooled immediately during mixing
LN40-60	100.0	42.4	Cooled 60 minutes after mixing

6.2.2 Results of Delayed Dosing on Setting Time

ASTM C 403, "Standard Test Method for Time of Setting of Concrete Mixtures by Penetration Resistance" (ASTM C 403, 2007), defines setting of concrete in terms of initial and final set. Initial and final set times are important because they give an indication of when the concrete can be properly placed, consolidated and finished. Time of set tests are performed on a mortar sample that is obtained by wet sieving fresh concrete and measuring the force required to penetrate needles of various sizes into the mortar. Initial and final set are achieved at a penetration resistance of 500 psi and 4000 psi, respectively.

To determine if the difference in set times was significant, the precision statement in ASTM C 403 was used, which states that the single operator range of results should not exceed 23% for initial set and 16% for final set.

The initial and final set time data in Figure 6.1 show a comparison between the setting times of concrete mixtures cooled with LN at different times and to varying

temperatures. The data bars in the setting time graphs show the overall time needed for each mixture to reach final set. The gray portion of the data bar shows the time required for each mixture to reach initial set. The black portion of the bar indicates the time required to go from initial set to final set.

Data presented in Figure 6.1 show that increasing the initial temperature of concrete reduces setting time (C100 compared to C73) and that decreasing the initial temperature increases setting time (LN40-00 compared to C73). These mixtures performed as expected. Cooling the mixture immediately to 73°F with LN resulted in setting times that were slightly longer than the control sample, but this difference could be the result of testing error and may not be significant. The data in Figure 6.1 also indicate that the delayed dosing of LN in mixtures LN73-15, LN73-45, and LN73-60 results in setting times similar to the control as well. Concrete cooling was delayed for up to 1 hour (LN73-60) and setting times were still similar to a 73°F mixture. This has implications on the concrete industry because ready-mix drivers can batch concrete at separate locations and cool the mixture at another location provided that dosing occurs within 1 hour of batching.

The results from mixtures LN40-00 and LN40-60 also have implications on the concrete industry. Currently, specifications by the Texas Department of Transportation prohibit the use of concrete with fresh temperatures below 50°F (TxDOT 420, 2004). This specification was designed to prevent the placement of concrete in cold weather which would result in slow setting times and strength gains. The data in Figure 6.1 show that concrete with a fresh temperature of 40°F does indeed have delayed setting time. However, since the ambient temperature is relatively high, the strength gain may not be adversely affected (as will be discussed in section 6.4). The delayed setting can be seen as an advantage. Excessive cooling can be used by concrete producers to purposefully extend setting times. For example, if a placement is at a considerable distance from the ready-mix plant, retarders can be used to delay setting in hot weather, but only buy a limited amount of time and in many cases can only be added at the time of batching. If the contractor has LN on site, cooling may be a cheaper and more effective way of extending setting. The data from LN40-00 and LN40-60 show that setting time is significantly prolonged when cooled to 40°F. Data from mixture LN40-60 illustrates that

even mixtures that are allowed to hydrate at 100°F for 1 hour may be cooled to 40°F and still experience prolonged setting times. This means that the mixture can even be cooled upon reaching the job site to prolong setting due to construction delays.

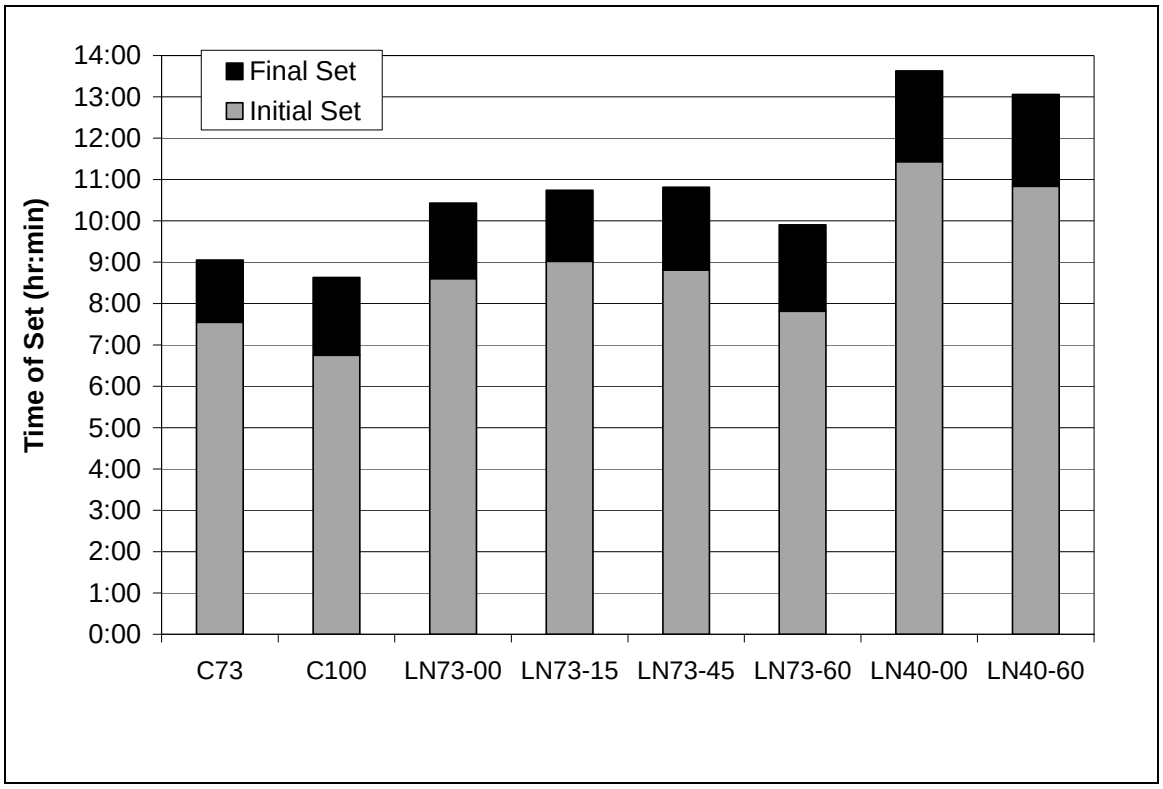


FIGURE 6.1 Initial and final set times for concrete mixtures delayed dosing mixtures

Table 6.2 shows the percent difference for the setting time between the control mixture and the LN mixtures. A positive percentage indicates that the LN mixture took longer to set than the control mixture, while a negative percentage indicates that the LN mixture set faster than the control mixture. Bold numbers denote that the mixture has exceeded the precision threshold in ASTM C 403. Concrete will show significant retardation in the setting time when concrete temperature is lowered to 40°F. The setting time results for mixtures C100, LN73-00, LN73-15, LN73-45, and LN73-60 were not statistically significant but did show a general trend of decreased setting time for C100 and increased setting times for all LN73 mixtures. In order to confirm the general trend

that concrete will take longer to set when cooled with LN, more testing would need to be done.

TABLE 6.2 Difference in Setting Times for Control and Liquid Nitrogen Mixtures

Mix	**Initial Set (23% max)**	**Final Set (16% max)**
	% difference between control and LN mixes	
C73		
C100	-10.6%	-4.6%
LN73-00	14.0%	15.2%
LN73-15	19.5%	18.7%
LN73-45	16.7%	19.5%
LN73-60	3.5%	9.4%
LN40-00	**51.5%**	**50.6%**
LN40-60	**43.6%**	**44.3%**

6.3 EFFECTS OF DELAYED DOSING ON CONCRETE STRENGTH

The compressive strength is the most common performance parameter used by engineers in the design of structures. Compressive strength testing results are primarily used to ensure that a concrete mixture meets the design strength specified by the engineer. Strength testing may also be used for quality control to verify the accuracy of mixture proportions, to schedule formwork removal, or to determine when to proceed with subsequent phases of a project. Since concrete strength is heavily dependent on cement hydration, LN dosing and the time at which dosing occurs may affect the rate at which concrete gains strength.

Splitting tensile strength is a mechanical property of concrete that is used in structural design. The direct application of tensile strength as a design parameter varies but is mainly used in the following design situations: shear strength and punching shear strength of slabs, bond anchorage, splicing of reinforcement, shear transfer in cracks, and minimum reinforcement. Tensile strength is equally important for unreinforced concrete structures that lack steel reinforcement to carry the tensile loads. As is the case with

concrete compressive strength, splitting tensile strength is heavily dependent on cement hydration and may be affected by LN dosing and the time that dosing occurs.

6.3.1 Compressive Strength

Testing for compressive strength is conducted in accordance with ASTM C 39, "Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens" (ASTM C 39, 2007). The test method consists of applying a compressive force along the cross-section of a cylindrical concrete specimen until failure occurs. Testing is conducted at various days to monitor the strength gain over time. The most important test occurs at 28-days, which is the strength that is used in design calculations and to ensure that the target strength was achieved. According to Building Code Requirements for Reinforced Concrete (ACI 318, 2005), concrete is considered acceptable as long as no single test is more than 500 psi below the design strength and the average of three consecutive tests equals or exceeds the design strength. The research presented in this section compares the compressive strengths of concrete mixtures cooled with LN at different times and to varying temperatures.

6.3.1.1 Results of Compressive Strength Testing

Figure 6.2 shows the 28-day compressive strengths for all mixtures. Table 6.3 shows the percent difference for 28-day compressive strengths between the control mixture (C73) and the LN73 mixtures. A positive percentage indicates that the LN mixture was stronger than the control mixture, while a negative percentage indicates that the LN mixture was weaker than the control mixture. Bold numbers denote that the mixture has exceeded the precision threshold in ASTM C 39. ASTM C 39 states that tests results of the same batch should not differ by more than 7.8%, which will be the threshold that identifies statistically significant results in compressive strength.

Most of the variables examined had no effect on the 28-day compressive strength. The high and low fresh temperatures (100°F and 40°F, respectively) did not affect the 28-day strength. Therefore, overdosing fresh concrete with LN appears to have no impact on

28-day concrete compressive strength. Furthermore, delaying the application of LN for an hour and then cooling the mixture to 40°F also had no effect on the compressive strength of the concrete mixture. Likewise, delayed cooling to 73°F with LN (LN73-15, LN73-45, LN73-60) did not affect 28-day compressive strength.

It appears that the 28-day compressive strength of mixture LN73-00 was slightly outside of the allowable range of error for this particular testing method. This appears to be inconsistent with the rest of the data gathered from the other mixtures. Since the criterion for this test is to compare concrete of the same batch and these are sample from different batches, more variation is expected. However, the general trend appears to be that delayed dosing and the temperature to which the concrete is cooled do not significantly affect the 28-day compressive strength of concrete.

Additional compressive strength data for 1-day and 7-day tests are shown in Appendix H. The compressive strength results for 1-day and 7-day tests are consistent with those from 28-day testing. However, one anomaly exists in the 1-day compressive strength graph. The compressive strength for the control mixture was disproportionately higher than the LN mixtures and was not consistent with compressive strength development at 7-days and 28-days. Nevertheless, there was no trend that suggested any differences in early-age strength of concrete cooled with LN.

TABLE 6.3 Difference in 28-day Compressive Strength

Mix	**Difference in 28-day compressive strength (7.8% max)**
C73	
C100	1.9%
LN73-00	**10.3%**
LN73-15	1.1%
LN73-45	-0.2%
LN73-60	4.2%
LN40-00	3.3%
LN40-60	5.7%

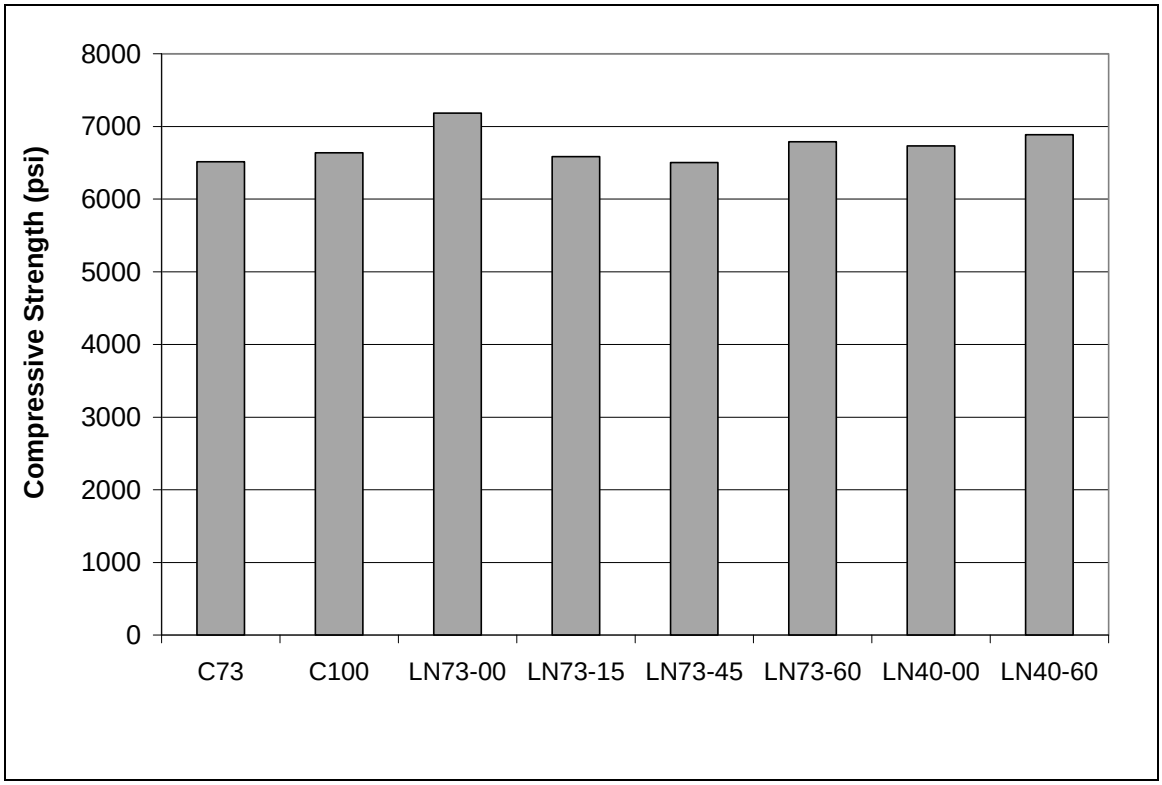


FIGURE 6.2 28-day compressive strengths for delayed dosing mixtures

6.3.2 Splitting Tensile Strength

Testing for splitting tensile strength is conducted in accordance with ASTM C 496, "Standard Test Method for Splitting Tensile Strength of Cylindrical Concrete Specimens" ASTM C 496, 2007). The test method consists of applying a compressive force along the length of a cylindrical concrete specimen until failure occurs. This type of loading creates tensile stresses on the plane containing the applied load and compressive stresses immediately around the applied load. Tensile failure occurs since the specimen is in a state of triaxial compression, allowing it to withstand higher compressive forces than would be possible by a uniaxial compression test. Plywood strips are used to apply a uniform load along the entire length of the cylinder. The maximum load is divided by appropriate geometrical factors to obtain the splitting tensile strength. The research presented in this section compares the splitting tensile strengths of concrete mixtures cooled with LN at different times and to varying temperatures.

6.3.2.1 Results of Splitting Tensile Strength Testing for Laboratory Mixed Concrete

28-day splitting tensile strength data are presented in Figure 6.3. Table 6.4 shows the percent difference in 28-day splitting tensile strength between LN mixtures and control mixtures. A positive percentage signifies that the LN mixture has a higher splitting tensile strength than the control mixture. Conversely, a negative percentage indicates that the LN mixture has a lower splitting tensile strength than the control mixture. Bolded numbers denote that the mixture has exceeded the precision threshold in ASTM C 496. The threshold that identifies statistically significant results in splitting tensile strength was found in ASTM C 496, which states that tests results of the same batch should not differ by more than 14.0%.

It was expected that the LN73 mixtures would be similar to the control mixture (C73), as in the compressive strength testing. However, mixtures LN73-00, LN73-60, and LN40-60 showed significant increases in splitting tensile strength while mixtures LN73-15, LN73-45, and LN40-00 showed slight decreases in splitting tensile strengths, but not significantly weaker than the control mixture (C73). Therefore, the general trend from the data seems to conclude that delayed dosing and overdosing of LN will not significantly affect the splitting tensile strength of concrete.

TABLE 6.4 Difference in 28-day Splitting Tensile Strength

Mix	Difference in 28-day splitting tensile strength (14% max)
C73	
C100	2.1%
LN73-00	**15.5%**
LN73-15	-2.9%
LN73-45	-5.2%
LN73-60	**16.3%**
LN40-00	-11.9%
LN40-60	**15.6%**

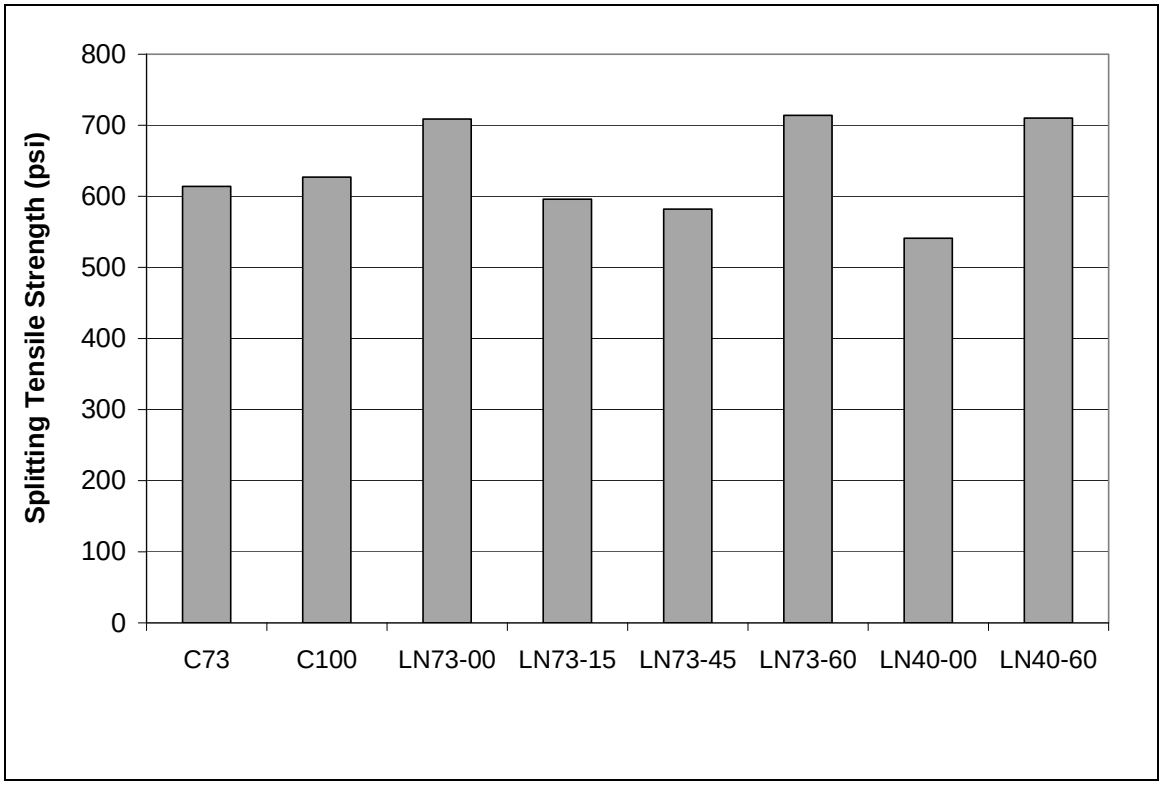


FIGURE 6.3 28-day splitting tensile strengths for delayed dosing mixtures

6.4 CONCLUSIONS

Setting time data presented showed that concrete producers can delay LN dosing for up to 1 hour and still expect setting times to be similar to a 73°F mixture. Therefore, ready-mix drivers can batch concrete at separate locations and cool the mixture at another location, or on-site, provided that dosing occurs within 1 hour of batching. In addition, setting time data showed that LN can be used to make concrete colder so that travel times of ready-mix trucks to job sites can be extended without having their loads rejected. Furthermore, setting time data showed that delaying setting of concrete at a job site by reducing the temperature would allow contractors to put trucks "on hold" during construction delays without losing trucks or sacrificing performance. The general trend indicated that concrete will take slightly longer to set when cooled with LN, but confirmation of this trend would need further investigation. Concrete will show

significant retardation in the setting time when concrete temperature is lowered to 40°F. Even mixtures that are allowed to hydrate at 100°F for 1 hour may be cooled to 40°F and still experience prolonged setting times. This has implications on the construction industry as well, as producers can cool the mixtures very cold for long hauls or construction delays and the cooling can be done on-site rather than at the batch plant.

The 28-day compressive strengths of concrete are relatively unaffected by delayed dosing and overdosing of LN. Splitting tensile strength was expected to be similar to compressive strength data, but there was much more variation in these results. This variation is likely due to the test method and not to actual variations in the splitting tensile strength of the specimens. It can be concluded that delayed dosing and overdosing of LN does not significantly affect the splitting tensile strength of concrete.

CHAPTER 7: HARDENED AIR VOID ANALYSIS AND FRESH AIR CONTENT

7.1 INTRODUCTION

The deterioration of reinforced concrete is caused by a combination of physical and chemical processes. The original concrete quality is often the major factor that affects the rate at which a reinforced concrete structure deteriorates. Low quality concrete ultimately results in significant cracking, which allows for the ingress of moisture and harmful chemicals that accelerate the deterioration process. Throughout the United States, concrete deterioration is commonly a result of repeated freezing and thawing. Multiple applications of deicing salts exacerbate damage by accelerating cracking and surface scaling. The service life of concrete can be increased by improving the ability to endure repeated freezing and thawing cycles.

Small, closely spaced air bubbles in concrete are the primary method used to improve the freeze-thaw resistance of concrete. Air voids act as release valves for excessive pore water pressure that develop in the concrete due to the expansion of freezing water. During the freezing process, water expands causing pressure to develop that is in relation to the distance the water must travel to reach the nearest void. Therefore, having a closely spaced network of air bubbles reduces the likelihood that the pressure of freezing water will damage the concrete (Taylor et al., 2006).

The development of air entrainment in concrete is a function of temperature, aggregate gradation, mixing action, pumping, and finishing. Changes in any of these parameters may affect the amount and distribution of air that develops in concrete. A significant concern with using liquid nitrogen (LN) to cool concrete is the effect that it will have on air entrainment. Because LN is injected into the concrete mixer at such high pressures, there are concerns that the thrust of the nitrogen spray will force air out of concrete mixtures. Furthermore, the effects of cryogenic temperatures on concrete may hinder the development of entrained air bubbles in fresh concrete. Since LN dosing occurs at the same time that air-entrained bubbles form, LN may interfere with bubble

formation. Several tests were performed to investigate the effects of LN on the air void system of fresh and hardened concrete. Fresh air content was measured by the pressure method as outlined in ASTM C 231, "Standard Test Method for Air Content of Freshly Mixed Concrete by the Pressure Method (ASTM C 231, 2004). The hardened air void system was examined for air bubble spacing factor and specific surface by the RapidAir 457 analyzer, which is manufactured by Concrete Experts International. Concrete mixtures for air void testing incorporated various supplementary cementing materials and chemical admixtures.

7.2 BACKGROUND

Air-entraining admixtures are chemical liquids that are used to stabilize air bubbles in a concrete mixture by reducing the surface tension at the air-water interface (Taylor et al., 2006). The liquid is poured directly into a concrete mixture either before or shortly after mixing begins. The shearing action created by the mixer and aggregates entrains and divides air into millions of tiny bubbles by causing a soap-like layer to form around the air bubbles. It is very important that sufficient mixing time be allowed to generate and stabilize the air bubbles (Taylor et al., 2006).

Air bubbles are classified into two different categories, entrapped and entrained. Entrapped air bubbles are fairly large and measure approximately 1 to 10 millimeters (mm) or more in diameter. These types of bubbles are too large and spaced too irregularly to be of any benefit in reducing freeze-thaw damage. Only entrained air is effective in reducing the internal stress within concrete. Entrained air bubbles are much smaller voids that measure from 0.01 mm to 1 mm in diameter and are uniformly distributed throughout the paste (Atkins, 2003).

The air void system in concrete can be described using several characteristics such as air volume, spacing factor, and specific surface. Air volume is the most commonly specified characteristic but it does not give any indication as to the size or distribution of the air voids. It simply gives a measurement of the total volume of air in a concrete mixture. In general, the air content of entrained concrete is typically given as 6% ± 1% by volume. With the development of new technology, measuring air void

networks has become much easier and have allowed for the measurement of air bubble spacing factor and specific surface.

Bubble spacing factor is an empirically developed number that represents the maximum distance that water would have to travel in the cement paste to reach an air void. Concrete deterioration due to freezing and thawing is not a concern as long as the distance between air bubbles is less than the critical maximum distance at which excessive stresses develop. A bubble spacing factor less than 0.008 in. has been shown to provide adequate resistance to freezing and thawing.

Specific surface is a ratio of the total bubble surface area to the volume of air. The ratio gives a general idea as to the relative number and sizes of the air voids and is expressed in in^2/in^3 or in^{-1}. Specific surface is, therefore, an indicator of the efficacy of an air void system. A high specific surface area indicates a greater number of small air voids that provide more protection than larger air voids since there are more air bubbles and the distance between them is smaller. Concrete with a specific surface greater than 610 $in.^{-1}$ has been shown to perform adequately in areas of freezing and thawing.

7.3 EXPERIMENTAL METHODS

The concrete testing matrix in Table 3.5 was developed to incorporate supplementary cementing materials (SCMs) and chemical admixtures that may be found in hot weather concreting and mass concrete applications. In addition, combinations of SCMs and chemical admixtures were included to determine if LN would affect them differently when combined. Each individual mixture was prepared twice so that a control and a LN mixture could be compared to each other. The control mixtures were comprised of mixing materials that were stored at 73°F, mixed at 73°F, and cured at 73°F. The LN mixtures were comprised of mixing materials stored at 100°F, mixed at 100°F, and then cooled to 73°F with LN. It should be noted that mixtures 08 and 16 - 20 are the only mixtures that contain air entraining admixture. A cement oxide analysis and aggregate gradations for the subsequent tests are shown in section 3.3.1 in Tables 3.3 and 3.4.

7.4 FRESH AIR CONTENT BY PRESSURE METHOD

Measuring the air content of fresh concrete by the pressure method is common because of the simplicity and the short amount of time involved in testing. The test method is performed using an air meter, as shown in Figure 7.1, specified in ASTM C 231.

FIGURE 7.1 Pressure meter used to measure the air content of fresh concrete

Measuring air content of fresh concrete is based on principles employing Boyle's law, which states that an increase in external pressure causes a volume reduction that is proportional to the amount of air in the sample. Since concrete is comprised of incompressible materials, except for air, the quantity of air in the sample can be calculated by measuring the resultant volume change as the external pressure is increased.

7.4.1 Results of Fresh Air Content by Pressure Method

The results in Figure 7.2 show the air contents of 20 laboratory concrete mixtures. Of the 20 mixtures, 11 experienced a decrease in air content when dosed with LN, 4 other

mixtures actually experienced an increase in air content and 5 mixtures experienced no change in air content. ASTM C 231 states that the air contents of the same batch should not differ by more than 0.8% air by volume of concrete, which will be the threshold that identifies statistically significant results in air content. Data presented in Table 7.1 show that none of the results for air content were statistically significant except for the air-entrained concrete mixtures. The mixtures with bold faced numbers indicate concrete mixtures where the air content difference between the control and LN mixtures were greater than 0.8% air. A positive value means that the LN mixtures had more air than the control mixtures while a negative value means that the LN mixtures had less air than the control mixtures. Since none of the non-air-entrained mixtures showed statistically significant results, the remainder of this section will focus on discussion of the air-entrained mixtures.

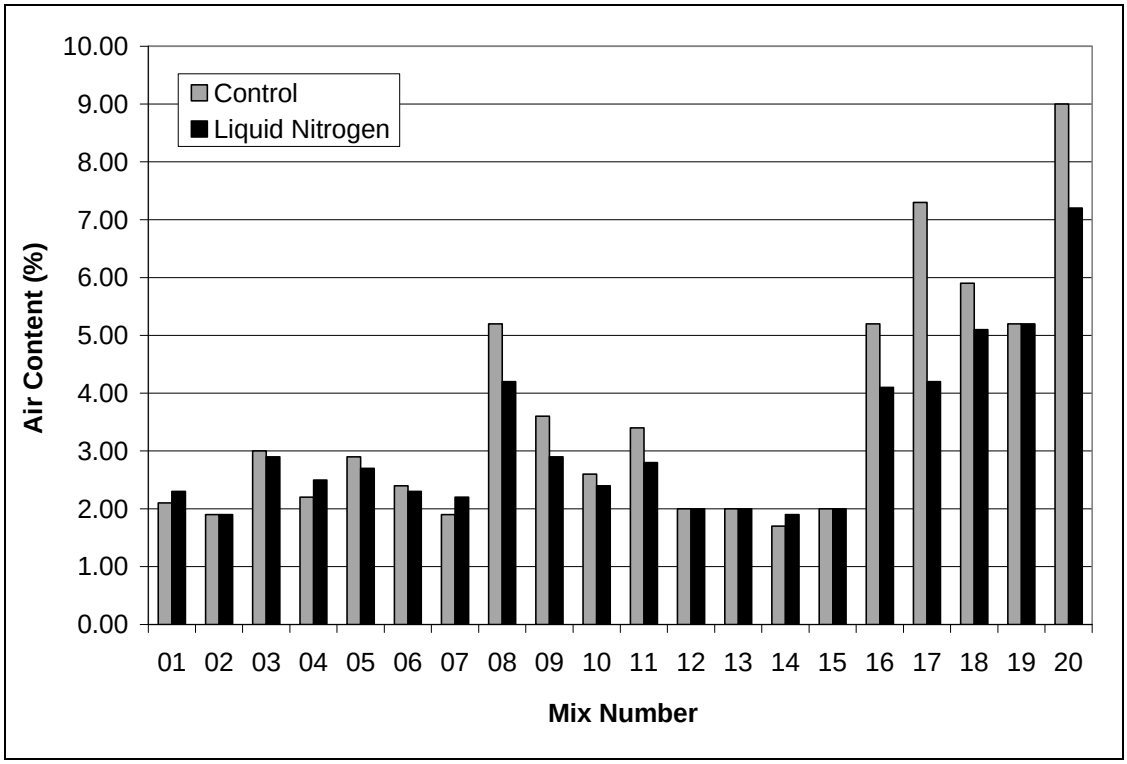


FIGURE 7.2 Fresh air contents for laboratory-mixed concrete

TABLE 7.1 Air Content Differences between Control and Liquid Nitrogen Mixtures

Mix ID	Actual difference in air content between control and LN mixes (%)
1	0.2
2	0.0
3	-0.1
4	0.3
5	-0.2
6	-0.1
7	0.3
8	**-1.0**
9	-0.7
10	-0.2
11	-0.6
12	0.0
13	0.0
14	0.2
15	0.0
16	**-1.1**
17	**-3.1**
18	**-0.8**
19	0.0
20	**-1.8**

The air-entrained mixtures that were dosed with LN experienced statistically significant reductions in air content, except for mixture 19 (Class C fly ash, water reducer, air entrainer), which showed negligible effects. Some of the reductions in air content were quite significant with the smallest reduction being 0.8% air and the largest reduction being 3.1% air. Therefore, it appears that air-entrained concrete mixtures may lose considerable air during LN application. This may possibly be caused by preheating of the mixing materials, which reduces the slump as discussed in Chapter 3 and consequently, the mixing action. As discussed earlier, the development of air bubbles is a function of multiple factors, such as temperature and mixing action. Therefore, a combination of temperature and mixing action may be at fault in reducing the amount of air contained in air-entrained concrete.

The non-air-entrained concrete mixtures did not show the same loss of air as did the air-entrained mixtures. Mixtures 01 - 07 and 09 - 15 show variable results with increases, decreases, and no change in the air contents of control and LN mixtures. There was relatively little change in the results and none of them were statistically significant. Part of this may be attributed to the fact that non-air-entrained concrete does not really contain that much air to begin with and is therefore relatively unaffected. In addition, non-air-entrained concrete does not use a sensitive admixture that is dependent upon stable temperatures and consistent mixing action.

7.4.2 Fresh Air Content of Field Mixed Concrete

Additional air content testing was performed on concrete mixtures from ready-mix trucks to determine if the results from laboratory testing agreed with results from field testing. Field-mixed concrete was sampled from concrete trucks at the Transit Mix batch plant in Round Rock, Texas. Sampling occurred in August 2006 on concrete that was to be used as rip rap to stabilize the sides of an open channel waterway. The ambient temperature was approximately 105°F, which necessitated the use of LN for mass concrete, bridge decks, and pavements to ensure that they met temperature specifications. Rip rap concrete does not a have a temperature specification and it was not necessary to dose the concrete with liquid nitrogen. However, Transit Mix dosed the rip rap concrete anyway to assist in the research. Concrete was discharged into a wheelbarrow before LN dosing and again after LN dosing was complete. This is different than the testing that was conducted in the laboratory. In the lab, air content testing was always conducted on concrete that was at 73°F. Control mixtures were stored and mixed at 73°F and LN mixtures were preheated to 100°F and then cooled to 73°F before air content testing. With the field testing, it was impossible to keep the control mixtures at 73°F since the materials were stored outside in the hot sun. Therefore, air content was measured on hot concrete mixtures before LN dosing occurred and then on the same mixture after LN dosing had occurred. The comparison of these results do not correlate directly to laboratory mixed concrete but these results are the only that are available in the field.

Two wheelbarrows of concrete were taken from four ready-mix trucks. The first set of wheelbarrows consisted of uncooled concrete that was between 93°F to 99°F. Air content testing was performed with a concrete pressure meter immediately upon sampling. The concrete trucks were then dosed with LN and the second set of wheelbarrows consisted of cooled concrete that was between 65.1°F to 81.8°F. Again, air content testing commenced immediately upon sampling the cooled concrete. All of the concrete used in field testing was air-entrained.

Although the air contents in Figure 7.3 appear somewhat high, they were taken from the ready-mix trucks immediately after the mixer was charged. Since concrete producers have to take into account temperature, travel time, and finishing techniques, concrete is often produced with very high air contents so that upon arrival at the jobsite, the air content will be as ordered. Therefore, the air contents in Figure 7.3 are high since the ready-mix truck had yet to travel to the jobsite and deliver its load.

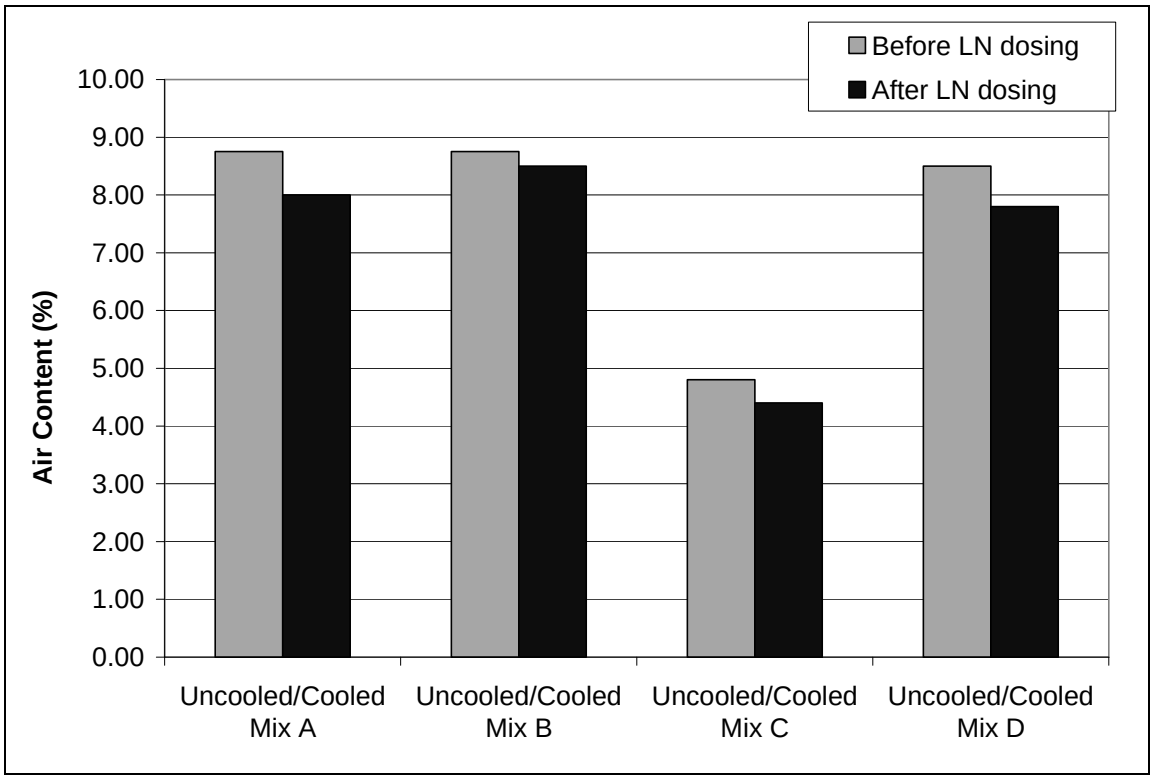


FIGURE 7.3 Fresh air contents for field-mixed concrete

The results of air content testing of field-mixed concrete show that air-entrained concrete experienced a reduction in air content with liquid nitrogen use in all four mixtures. None of the reductions in air content were statistically significant since the smallest reduction was 0.25% air and the largest reduction was 0.75% air. However, the general trend from field-mixed concrete appears to be that fresh concrete will lose a little air from the mixture when dosed with LN. This discrepancy may be due to differences in the types of samples tested in the lab and in the field. Control samples in the lab had all materials stored at 73°F, while LN samples were cooled to 73°F from 100°F. In the field, control samples were 93°F to 99°F at the time of casting and LN samples were 65.1°F to 81.8°F. This fresh temperature is unlikely to make such as significant difference on air content, especially since all samples were cured in a controlled-temperature environment, but is worth considering.

The reduction in air may also be caused by preheating of the mixing materials as well as decreased slumps, which affect the mixing action of concrete. Adequate mixing is essential in developing air bubbles and these two factors reduce the fluidity of concrete in such a way that, perhaps, less air bubbles are being stabilized.

7.5 HARDENED AIR VOID ANALYSIS

The air content of hardened concrete specimens was performed with a RapidAir 457 Automated-Air-Void-Analyzer, which is manufactured by Concrete Experts International. The instrument has an automated image analysis system (Figure 7.4) that evaluates the air void network of hardened concrete according to the linear traverse method explained in ASTM C 457, “Standard Test Method for Microscopical Determination of Parameters of the Air-Void System in Hardened Concrete” (ASTM C 457, 1998). Previously, trained technicians were required to use a microscope to analyze the pore structure of concrete; this method normally required 4 to 6 hours to perform. The analysis time required with the RapidAir 457 Automated-Air-Void-Analyzer is only 15 minutes and provides measured parameters such as total air content, spacing factor, and specific surface.

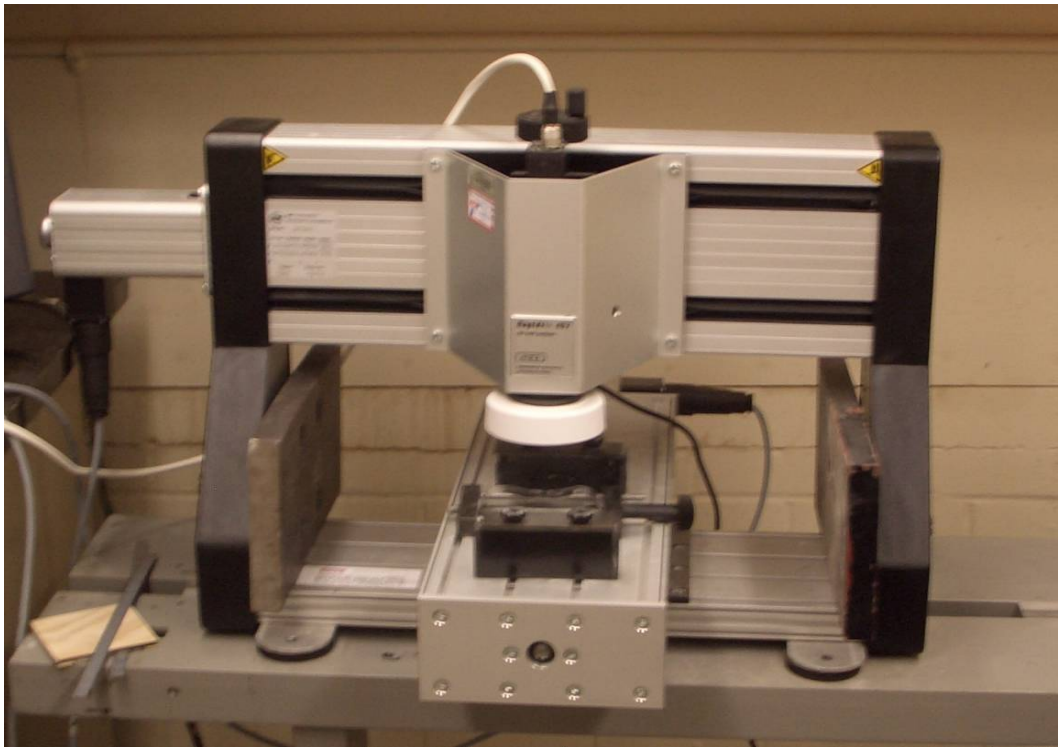


FIGURE 7.4 RapidAir 457 Automated-Air-Void-Analyzer

Hardened air void specimens were fabricated from Chinese take-out boxes (dimensions: 4.75 in. long, 3.75 in. wide and 4.00 in. high) and some concrete cylinders. Originally, only concrete specimens fabricated from Chinese take-out boxes were to be used for hardened air void testing. The boxes provided similar dimensions to those required for hardened air void specimens and would eliminate two difficult cuts of a concrete cylinder by a water saw. However, the preparation of each hardened air void specimen required several hours of polishing and, at times, some of the specimens were damaged. Therefore, concrete cylinders from the same mixture had to be used in their place.

Concrete specimens were taken from mixtures 16 (air entrainer, water reducer), 17 (air entrainer, water reducer, silica fume), 18 (air entrainer, water reducer, Class F fly ash), 19 (air entrainer, water reducer, Class C fly ash), and 20 (air entrainer, water reducer, slag), as shown in Table 7.2 and sliced to obtain a thin rectangular section of concrete. The specimens were ground and lapped to obtain a plane, smooth surface that

was free of any sharp edges. The lapping quality was checked with a stereomicroscope. A contrast enhancing technique was used where the surface of the concrete specimen was colored black with a permanent marker and then pounded with white powder to fill the voids. This type of surface facilitates maximum precision and identification of all air voids present in the concrete. Finally, any aggregates voids or noticeable cracks were colored black under the stereomicroscope so they were not counted as part of the air void system in the concrete paste. A photograph of a fully prepared specimen is shown in Figure 7.5. The entire lapping and specimen preparation process took approximately 30 minutes for each individual specimen. At this point, the specimen was loaded in the RapidAir system and was analyzed.

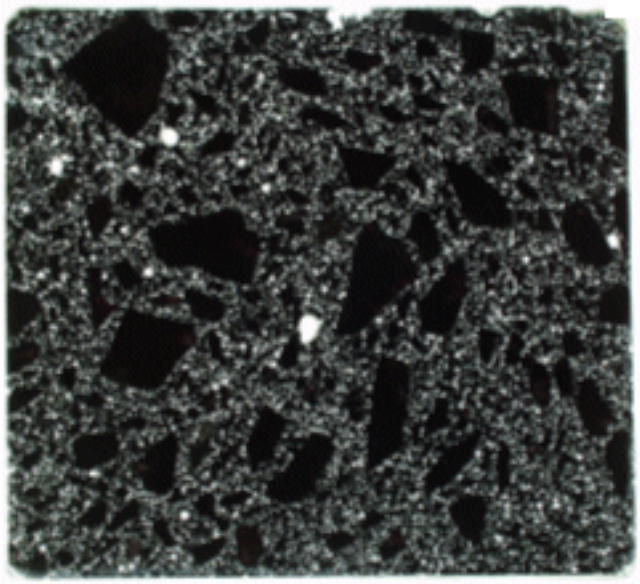


FIGURE 7.5 Fully prepared concrete specimen for air void analysis

7.5.1 Air Void Analysis of Hardened Concrete Specimens

The RapidAir 457 air void analyzer was used to measure the 10 different concrete samples (mixtures 16-20) for air content, specific surface, and spacing factor. Five of the samples were control specimens where all the mixing materials were stored at 73°F and

mixed at 73°F. The remaining five samples were identical specimens except that the mixing materials were stored at 100°F, mixed at 100°F, and then cooled with LN to 73°F.

The data shown in Table 7.2 compares the control and LN mixtures for the five concrete mixtures. The composition of each mixture can be found in Table 3.5; all mixtures were air-entrained. Table 7.2 provides data for fresh air content, hardened air content, specific surface, and spacing factor for each sample along with the percent difference between the control and LN samples for each mixture. A positive percentage indicates that the LN mixture has higher air content (fresh or hardened), a higher specific surface, or a greater spacing factor. A negative percentage indicates the contrary.

TABLE 7.2 Hardened Air Void Measurements

Mix ID	Fresh Air Content (%)	Difference in air content (% air)	Hardened Air Content (%)	Difference in hardened air content (% air)	Specific Surface (in^{-1})	Difference in specific surface	Spacing Factor (in)	Difference in spacing factor
C16 **LN16**	5.20 4.10	-1.10	4.48 5.22	0.74	627.4 574.7	-8.4%	0.0078 0.0080	2.6%
C17 **LN17**	7.30 4.20	-3.10	4.70 3.26	-1.44	463.3 533.5	15.2%	0.0103 0.0107	3.9%
C18 **LN18**	5.90 6.71	0.81	6.40 4.56	-1.84	767.4 952.1	24.1%	0.0054 0.0052	-3.7%
C19 **LN19**	5.20 6.10	0.90	3.95 3.79	-0.16	561.5 673.2	19.9%	0.0094 0.0080	-14.9%
C20 **LN20**	9.00 7.20	-1.80	5.96 3.74	-2.22	491.3 511.0	4.0%	0.0089 0.0105	18.0%

The data in Table 7.2 show considerable differences between the fresh air content and the hardened air content of each individual sample. Most likely, these discrepancies can be attributed to handling, placement, consolidation, and finishing, which occurs after the fresh air content is measured. Therefore, the handling and finishing techniques of concrete cause some of the air to be expelled from the concrete.

The hardened air content data show that the LN mixtures had less air than the control mixtures in 80% of the cases. Mixture 16 was the anomaly and actually showed a 0.74% increase in the air content of the LN mixture. The precision statement in ASTM C 457 states that the single operator, single lab range of two test results should not differ by more than 0.82% air. The differences in hardened air content are significant for mixtures 17, 18, and 20. It appears from the hardened air content data that concrete cooled with LN experiences a loss of air when compared to the control mixture. Perhaps, this difference may be caused by consolidation techniques for in-place concrete. Also, when LN mixtures are discharged from the mixer, there is often a loss of slump, as shown in Chapter 3. This requires additional agitation in order to place and finish the concrete, which may lead to an additional loss of air.

Specific surface data show an increase in the specific surface of LN mixtures in 80% of the cases. However, mixture 16 was again the anomaly and showed an 8.4% decrease in the specific surface of the LN mixture. As stated earlier, a high specific surface area indicates a greater number of small air voids that provide more protection against freezing and thawing. As well, a specific surface greater than 610 $in.^{-1}$ has been shown to perform adequately in areas of freezing and thawing. Although there was an increase in the specific surface for mixtures 17 - 20, it appears that the increase is a function of the decreasing air content rather than increasing bubble surface area. Since this parameter is a ratio, the specific surface is inversely proportional to the air content. By comparing the air content with the specific surface, it is evident that the reason for the increase in specific surface for mixtures 17 - 20 and the decrease in mixture 16 was the inverse proportionality of the two parameters.

The most important parameter for freezing and thawing resistance is the spacing factor. A spacing factor of 0.008 in. or less has been shown to provide adequate freezing and thawing resistance (ASTM C 457, 1998). The data in Table 7.2 show that the

spacing factor is affected in two of the mixtures (19 and 20) but relatively unchanged for mixtures 16 - 18. The precision statement in ASTM C 457 states that the single operator, single lab range of two test results should not differ by more than 22.6%. Based on the precision data, none of the data for spacing factor are statistically significant, indicating that LN does not affect the spacing factor of concrete.

7.6 CONCLUSIONS

Fresh air content results of laboratory-mixed concrete showed that LN generally lowered the air content for air-entrained concrete mixtures. This may possibly be caused by preheating of the mixing materials, which reduces slump and consequently, mixing action. Therefore, a combination of temperature and mixing action may be at fault in reducing the amount of air contained in air-entrained concrete. The non-air-entrained concrete mixtures did not show the same loss of air as did the air-entrained mixtures. Part of this may be attributed to the fact that non-air-entrained concrete does not really contain that much air to begin with and is therefore relatively unaffected. In addition, non-air-entrained concrete does not use a sensitive admixture that is dependent upon stable temperatures and consistent mixing action.

The results of air content testing of field-mixed concrete show that air-entrained concrete experienced a reduction in air content in all four mixtures. None of the reductions in air content were statistically significant since the smallest reduction was 0.25% air and the largest reduction was 0.75% air. However, the general trend from field-mixed concrete appears to be that fresh concrete will lose a little air from the mixture when dosed with LN.

The hardened air content data show that LN mixtures had less air content than control mixtures in 4 out of 5 cases, with the difference being statistically significant in three of these. The data from hardened air void testing also show a loss of air content for in-place concrete as compared to fresh concrete and that LN does not affect the spacing factor of concrete. Results for specific surface measurements show that although there was an increase in the specific surface for mixtures 17 - 20, it appears that the increase is a function of the decreasing air content rather than increasing bubble surface area.

CHAPTER 8: TEMPERATURE READINGS OF STEEL MIXING DRUMS

8.1 INTRODUCTION

Certain ductile metals experience a drastic loss in tensile ductility when exposed to cryogenic liquids, such as liquid nitrogen (LN). Steel is sensitive to temperature and will behave in a brittle or ductile manner depending on how hot or cold the material becomes. Higher temperatures allow planes of atoms to slide across one another when a stress is applied, making steel more ductile. As temperature decreases, it becomes more difficult for this slip to occur. The atoms in the crystal lattice cannot slide, causing fracture to occur in a brittle manner.

A significant concern with using LN to cool concrete is the sensitivity of steel mixing drums to the extreme temperatures of LN. At high temperatures, atoms in the crystal lattice of steel are mobile and allow dislocations in the crystal lattice to slide past one another. Bonds can reform around dislocated surfaces causing nearby lattices to distort and distribute stress. At low temperatures, cracks form since the atoms in the crystal lattice cannot slide past each other as easily. Cyclic thermal shock causes cracks to grow until they reach a critical fracture length. The cracks rapidly propagate through the metal and the material fractures. Concrete producers that have used LN to cool concrete have experienced cracking in the drums of some of their mixing trucks, as shown in Figures 8.1 and 8.2. Cracking in the mixing drums, however, has only proved to have minor consequences on operations since the mixing trucks were simply removed from service to weld the cracks back together. This does cause delays and some loss of revenue, but may also reduce the service life of the drum.

One concrete ready-mix company has actually shattered the entire mixing drum of one of their trucks, similar to glass shattering into tiny fragments. The mixing drum was beyond repair and was removed from the truck to be replaced with a new mixing drum (Johnson, 2006). Ironically, the mixing drum that shattered was a fairly new steel drum that had only been in service for several months. Anecdotal evidence reported by one

ready-mix company suggests that older mixing drums are no more susceptible to cracking than newer mixing drums (Johnson, 2006). Furthermore, all of the mixing drums that have cracked were carrying full loads of concrete, meaning that almost the entire surface of the mixing drum was insulated by the surrounding concrete. Cracking in the mixing drums has yet to follow any pattern with regard to load capacity or age of the mixing drum.

FIGURE 8.1 Cracking on the mixing drum of a ready-mix truck

FIGURE 8.2 Cracking caused by liquid nitrogen dosing on a mixing drum fin

For many years, companies have been producing and storing LN in special steel tanks. Metallurgists have found that manipulating the composition allows steel to be more resistant to temperature. In the case of LN, steels high in nickel are more ductile at cryogenic temperatures. However, manufacturers of concrete mixing trucks have not used such high grade steel to produce mixing drums because, historically, there has not been a need for concrete mixing drums to resist cryogenic temperatures. In addition, nickel is very expensive and would greatly increase the manufacturing costs of each truck. Therefore, mild carbon steel susceptible to extreme temperatures is used to manufacture concrete mixing drums.

The use of LN to cool fresh concrete provides many advantages that are not possible with other cooling methods. The automated dosing procedures of LN allows for precise temperature control and eliminates the risk of injury to workers since the LN

injection system is completely separate of all operations and operated remotely, as shown in Figure 8.3. Research was conducted to determine the cause of cracking in concrete mixing drums subjected to applications of LN. The research focused on two definite factors that would most likely cause cracking in the drums: (1) quality of the steel and (2) extreme temperatures.

FIGURE 8.3 Cooling fresh concrete with liquid nitrogen

8.2 STEEL QUALITY

A metallurgical analysis was performed on steel fragments that were taken from a mixing drum that had cracked due to LN dosing. The analysis was performed on the samples to determine more about the properties of the steel used to fabricate drums and mixing fins. Three steel specimens were sent to Chicago Spectro Service Laboratory,

Inc. in Chicago, IL for a metallurgical analysis. Fracture-1 refers to a steel specimen that was removed from the fracture zone of the mixing drum. The other two specimens sent in for analysis (Control-1, Control-2) were control specimens that were removed from mixing drums that had not fractured, but were out of service. The compositional analysis for each specimen is shown in Table 8.1

Results of the analysis show that the mixing drums were most likely manufactured with scrap metal. Some of the individual metals present in the mixing drums, such as copper and nickel, are not metals that are added to improve the quality of the steel. Most likely, those metals were already present in the scrap steel that was used to fabricate the mixing drum. Furthermore, the analysis shows that the high carbon contents found in all three specimens made the mixing drums very brittle and thus susceptible to cracking. Cracking typically occurred towards the top of the mixing drum, in the vicinity where the LN lance is inserted into the drum. Crack propagation followed no distinct path, indicating that cracking is most likely not a thermal fatigue issue but rather a brittle fracture that propagates at high velocities.

TABLE 8.1 Steel Compositions of Concrete Mixing Drums

	Sample ID / Description		
Element Name	**Control-1**	**Control-2**	**Fracture-1**
Carbon	0.31	0.33	0.35
Manganese	1.24	1.18	1.21
Phosphorous	0.015	0.017	0.015
Sulfur	< 0.005	< 0.005	< 0.005
Silicon	0.20	0.19	0.19
Nickel	0.10	0.12	0.13
Chromium	0.16	0.16	0.06
Molybdenum	0.01	0.01	0.08
Copper	0.24	0.22	0.27
Aluminum	0.020	0.025	0.026

8.3 TEMPERATURE READINGS OF STEEL MIXING DRUMS

Steel mixing drums temperatures were monitored during LN dosing. Since steel becomes brittle at low temperatures, it was important to monitor locations on the mixing drum that would be susceptible to cracking. Temperature readings were taken by two different methods: infrared thermography and with iButton temperature sensors.

Initial attempts to record the temperature of steel mixing drums were conducted with an infrared camera. Immediately, it was discovered that an infrared camera would not be suitable for the measurements. The vapor caused by LN dosing encapsulated the entire mixing drum, causing the infrared camera to measure the temperature of the vapor and not the mixing drum. Numerous attempts were made to capture an unobstructed thermal image of the mixing drum. This was done by stopping the mixing, dosing temporarily, and allowing the vapor to dissipate before imaging. The resulting image is shown in Figure 8.4. The mixing truck in the photograph is not the same one from the thermal image; it is just an example truck that was used to show the location of the

thermal image. The red area on the left side of the image is the collar upon which the mixing drum spins. The orange and green area on the right side of the thermal image is part of the ladder frame. The blue and purple area between them is the mixing drum. Color schemes in the thermal image correspond to a temperature scale that is included in the image. Figure 8.4 shows that the temperature of the mixing drum was between 45°F and 55°F. Hand-held infrared thermometers at the time of the testing indicated that the temperature of the mixing drum was actually 15°F to 20°F colder. Some of the error in the thermal images can be attributed to radiated heat caused by the sun. Another source of error was the high relative humidity the day of testing. Apparently, the infrared camera was detecting the thermal changes of the water vapor in the air. Therefore, better temperature sensors were needed in order to capture the true temperature of the mixing drums.

In order to record the true temperature of concrete mixing drums, temperature sensors needed to be attached directly to the steel. However, the spinning motion of the mixing drum during LN dosing necessitated that the temperature sensors that had datalogging capabilities and an internal source of power since the temperature sensors could not be connected to an external computer without tangling a bunch of wires the moment that the mixer started to spin. iButton (Dallas Semiconductor, Inc.) temperature sensors were selected to monitor temperatures because of their size (approximately the circumference of a dime and 1/2-inch thick), internal power supply, and datalogging capabilities. A photograph of a iButton sensor is shown in Figure 8.5.

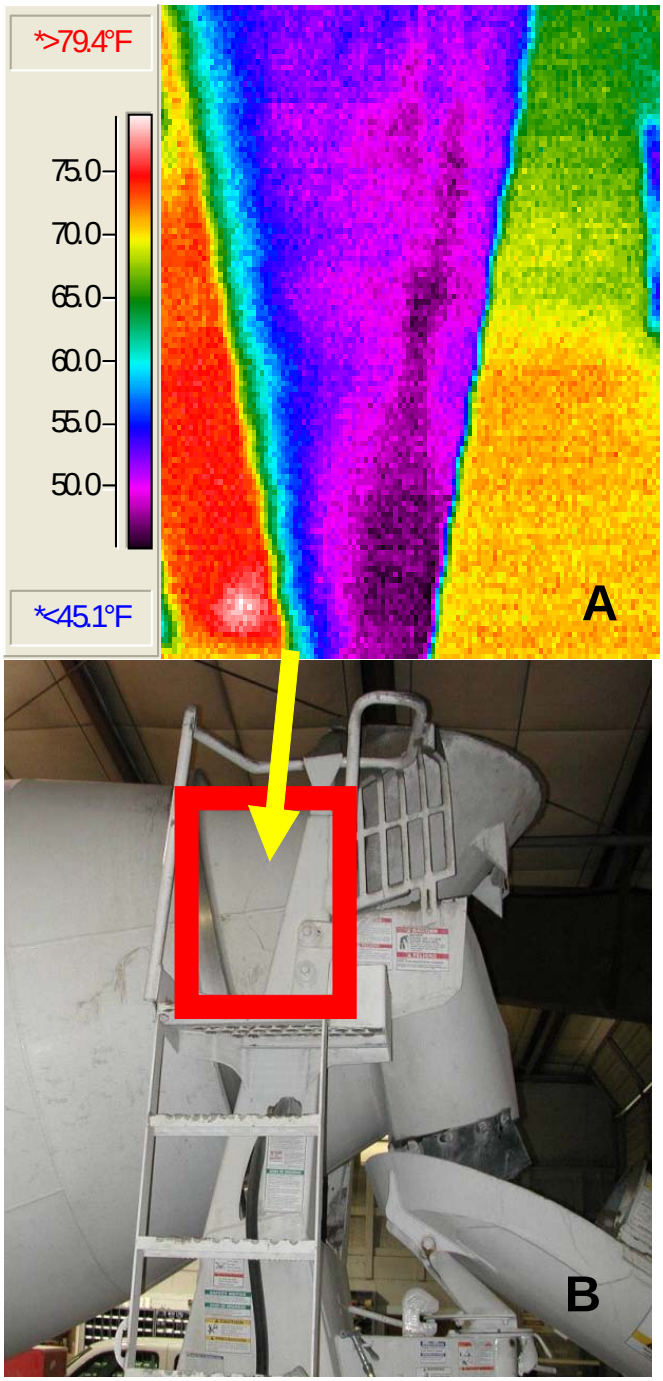


FIGURE 8.4 Thermal image (picture A) of a steel mixing drum during liquid nitrogen dosing. (Picture B indicates the area on a mixing drum that the image is capturing)

FIGURE 8.5 iButton temperature sensor

Temperature measurements were conducted with iButton sensors that were encased in a protective pinewood casing (Figure 8.6) to prevent the iButtons from taking temperature readings of the surrounding LN vapor, which is significantly colder than the steel mixing drums. The 3-inch square casing was lined with thin, high-powered magnets to ensure that the casing would not fall off the mixing drum during mixing. The only exposed part of the iButton was the surface that makes contact with the mixing drum (Figure 8.7) so that the true temperature of the drum was measured.

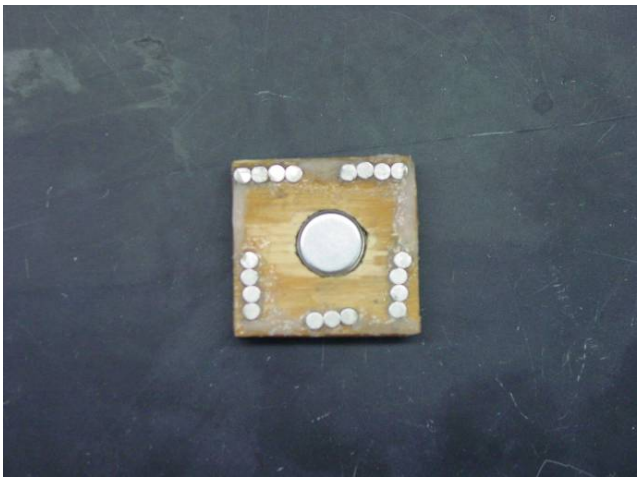


FIGURE 8.6 iButton temperature sensor in protective casing

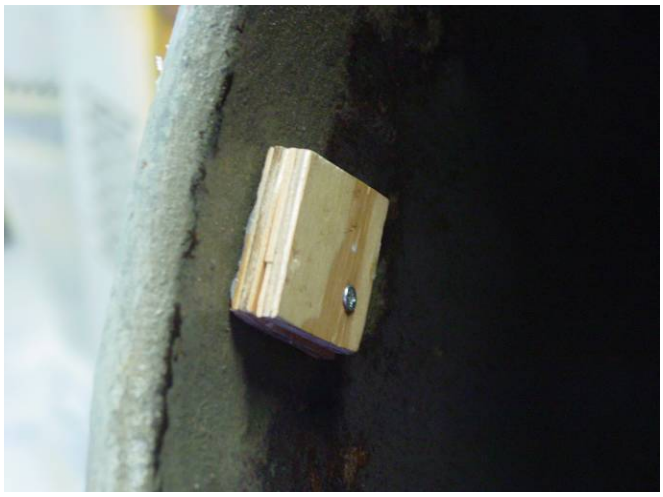


FIGURE 8.7 iButton sensor attached to the side of a laboratory mixing drum

Temperature sensors were placed just inside the opening of the mixing drum where cracking typically occurs. These areas provided the absolute coldest temperature that the steel drum would experience since they are nearest to the LN spray and uninsulated by concrete. Furthermore, placing the sensors at the top of the mixing drum protected the iButton casings from being ripped off the side of the mixer by spinning concrete.

The data in Figure 8.8 show temperature readings from two temperature sensors placed in the same truck. One temperature sensor was placed on the inside of the mixing drum and the other temperature sensor was placed on the outermost fin of the mixing drum. The sensors were placed in the mixing truck before LN dosing and then removed immediately following LN dosing. It is evident from the data that concrete mixing drums are highly susceptible to cracking due to the extreme temperatures encountered during LN dosing. The coldest temperature experienced by the mixing drum during one dosing application was -8.5°F and -15°F for the fin. This test was repeated four times on four different concrete mixing trucks and showed similar results with most of the temperature readings falling below 0°F. These results are shown in Appendix I. It should be noted that measurements were made on trucks where the lance was aligned correctly and could be significantly lower if the lance is misaligned.

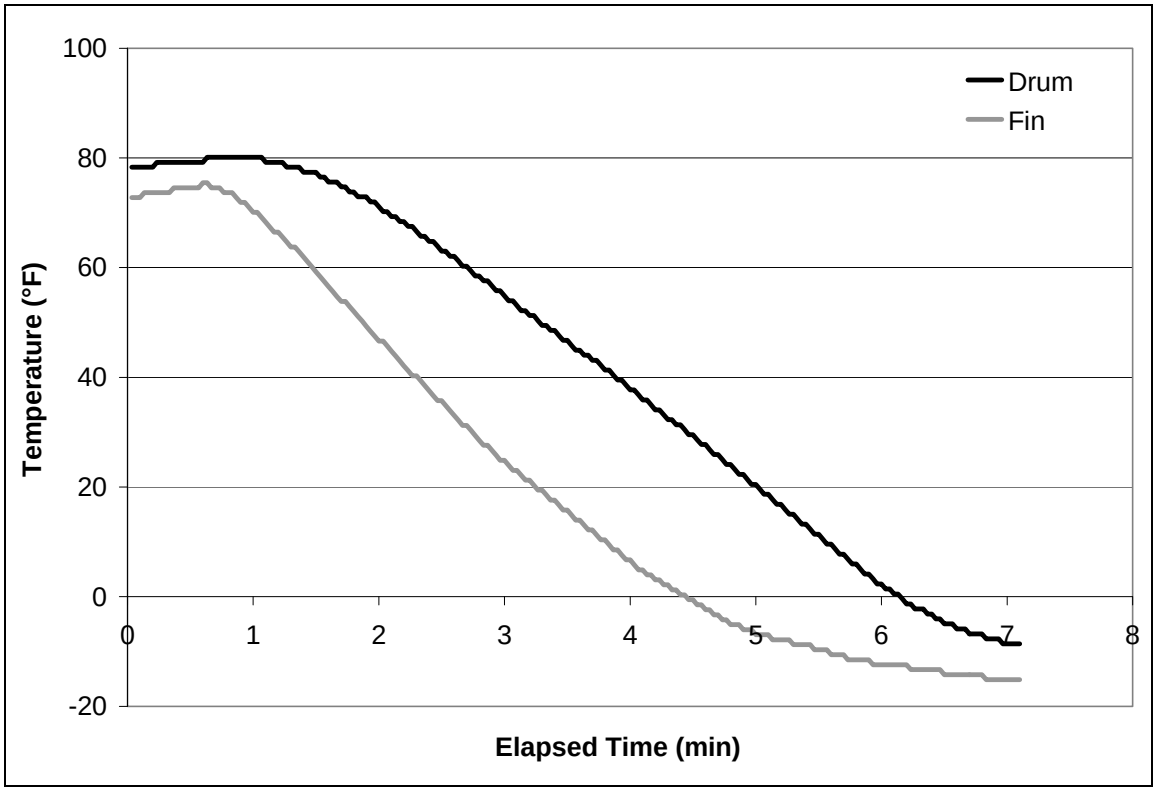


FIGURE 8.8 Temperature of mixing drum and fin during LN dosing (Truck 5)

8.4 CONCLUSIONS

A significant concern with using LN to cool concrete is the sensitivity of the steel mixing drums to the extreme temperatures of LN. Most mixing drums are made of mild carbon steel that are susceptible to cracking when subjected to stress at cryogenic temperatures. Reports of cracking in mixing drums have yet to follow any pattern with regard to load capacity or age of the mixing drum.

A metallurgical analysis was performed on steel fragments that were taken from a mixing drum that had cracked due to LN dosing. Results of the metallurgical analysis show that the steel used to fabricate the mixing drums were most likely manufactured with scrap metal. Furthermore, the analysis shows that the high carbon contents found in all three specimens made the mixing drums very susceptible to brittle failure. Cracking typically occurred towards the top of the mixing drum, in the vicinity where the LN lance

is inserted into the drum. Crack propagation followed no distinct path, indicating that cracking is most likely not a thermal fatigue issue but rather a brittle fracture that propagates at high velocities. It was hypothesized that cracking may be caused by misaligned LN lances that spray onto the fins and the sides of the mixing drum.

Temperature data from iButton sensors show that concrete mixing drums are highly susceptible to cracking due to the extreme temperatures encountered during LN dosing. The coldest temperature experienced by the mixing drum during one dosing application was -8.5°F and -15°F for the fin. Measurements were made on trucks where the lance was aligned correctly and could be significantly lower if the lance is misaligned.

Concrete mixing drums will always be susceptible to cracking given the present quality of steel that is being used to fabricate the drums along with the sub-zero temperatures to which the mixing drums are being exposed.

CHAPTER 9: CONCLUSIONS AND FUTURE WORK

9.1 CONCLUSIONS

The results of a comprehensive study investigating the effects of liquid nitrogen on concrete conclude that liquid nitrogen has minimal impact on the performance and microstructural development of concrete. Concrete performance was tested in terms of slump, setting time, yield, compressive and splitting tensile strength, elastic modulus, rapid chloride permeability, and hardened and fresh air void analysis. Microstructural development was monitored by isothermal calorimetry, semi-adiabatic calorimetry, x-ray diffractometry, inductively coupled plasma, and environmental scanning electron microscopy. Additional testing was performed on concrete mixing drums to determine the effects of liquid nitrogen on the durability of steel mixing drums.

While mortar flow was unchanged by liquid nitrogen (LN) cooling, concrete slump appeared to decrease for LN cooled concrete compared to a room temperature control. Further testing showed that slump loss was not, in fact, caused by LN dosing but by preheating of the mixing materials. In other words, the slump of LN-cooled concrete is the same as that of the original, hot concrete. The implication of this result on concrete production is minimal because the expected slump of the hot mixture and the slump of the LN-cooled mixture is the same.

Initial laboratory setting time tests indicated that the use of LN to cool concrete did not have a significant effect on the initial or final setting time of concrete. As well, the window of finishability, the time between initial and final set, remained unaffected in most cases. Setting time tests for concrete mixtures cooled to near-freezing temperatures showed greatly increased initial set times, final set times and windows of finishability. Therefore, overdosing a concrete mixture in the field could have significant construction and durability implications.

Follow-up testing on setting time examining the effects of delayed dosing showed that concrete producers can delay LN dosing for up to 1 hour and still expect setting times to be similar to a 73°F mixture. Cooling the concrete to 40°F significantly extends

setting time, even if mixtures are allowed to hydrate at 100°F for 1 hour and then cooled to 40°F. These discoveries have several implications on the concrete industry. For example, since cooling can be delayed, ready-mix drivers can batch concrete at separate locations and cool the mixture at another location, or on-site, provided that dosing occurs within 1 hour of batching. This minimizes the cost of installing LN dosing devices at every batch plant. Also, travel times of ready-mix trucks to job sites can be extended without having their loads rejected. Furthermore, delaying setting of concrete at a job site by reducing the temperature would allow contractors to put trucks "on hold" during construction delays without losing trucks or sacrificing performance.

The results of yield testing show negligible volume changes in concrete cooled with LN. Since the differences in yield were so small between the control and LNCC mixtures, and the differences were both positive and negative for the mixtures tested, it can be safely assumed that concrete yield will not be affected when LN is used for cooling.

Data showed that LN did not affect the compressive strength of mortar mixtures, even with chemical admixtures. The compressive strengths for cement mortar cooled with LN are comparable to the compressive strengths of the control, chilled water, and ice mixtures. On the other hand, compressive strength results at 28 days for laboratory-mixed concrete showed that, on average, the LN mixtures were 500 psi stronger than the control mixtures with 50% of the mixtures showing a statistically significant increase in strength. However, compressive strength testing of field-mixed concrete did not confirm the results of laboratory testing. For field mixtures, the compressive strengths for cooled and uncooled concrete were virtually the same. These discrepancies may be due to water loss from the laboratory mixer during cooling, decreasing the effective w/c and increasing strength. This is not a concern in the field because of the much lower surface-to-volume ratio of concrete in the mixer.

Splitting tensile results in laboratory mixed concrete showed that mixtures cooled with LN generally had slightly higher splitting tensile strengths than control mixtures, likely due to water loss during mixing. In field-mixed concrete, 1 out of 4 mixtures had a statistically significant difference in strength, but that happened to be a reduction in

strength, whereas all the laboratory mixtures were strength increases. Therefore, it is likely that LN has no effect on the splitting tensile strength of field concrete.

Follow-up strength testing on mixtures that received delayed doses of LN demonstrated that the 28-day compressive strengths and splitting tensile strengths of concrete are relatively unaffected by delayed dosing and overdosing of LN.

The elastic modulus of LN cooled mixtures should be proportional to strength; that is, as strength increases, so should elastic modulus. Based on results from strength testing, it was expected that the elastic modulus for LN cooled concrete would be slightly higher than the room temperature control. However, some of the LN mixtures had a higher elastic modulus and others had a lower elastic modulus. The results of elastic modulus testing are thus unclear.

Data from rapid chloride penetrability testing showed a slight, but probably insignificant reduction in the total electrical charge passed through LN cooled concrete. The slight reduction in penetrability may be due to the same artifacts that increased strength, namely water loss in the laboratory mixer.

Semi-adiabatic calorimetry testing and analysis of the curve-fitting parameters α, τ, and β showed that LN had very little effect on the rate of hydration of concrete samples. Isothermal calorimetry on cement pastes showed that the use of chilled water, ice, or LN to cool fresh cement paste does not affect the rate of heat evolution provided that cooling is simultaneous with mixing. However, if LN cooling is delayed for as little as 30 seconds after initial contact of water and cement then hydration is accelerated in these samples compared to control mixtures. The cause for the accelerated heat emission was due to preheating of mixture materials before LN application. This pre-heating allowed for the rapid dissolution and immediate formation of initial hydration products, which accelerated the rest of the cement hydration process. Therefore, if cooling with LN is not performed immediately, then the hydration process will be accelerated and cannot be reversed by subsequent cooling. This may explain why LN-cooled mixtures have similar slumps to hot mixtures.

X-ray diffraction (XRD) analysis for ettringite, calcium hydroxide, and monosulfoaluminate shows that LN mixtures developed the same quantities of hydration

products as control mixtures. Therefore, LN dosing does not appear to affect the formation of ettringite, calcium hydroxide, or monosulfoaluminate in cement paste mixtures.

Cement paste pore solutions analysis by inductively coupled plasma (ICP) for calcium, sulfur, and potassium showed that the dissolution and consumption of calcium, sulfate, and potassium ions in LN mixtures appear to be similar to the room temperature (73°F) control mixture. Therefore, LN dosing has no effect on these processes.

Results from environmental scanning electron microscopy (ESEM) were used to examine the presence and distribution of hydration products in LN cooled samples. The images all showed the presence of ettringite crystals growing in the cement matrix as well as a thin layer of calcium silicate hydrate covering cement grains. Because of the resolution limitations of the instrument, it was very difficult to image calcium hydroxide and ettringite. Based on ESEM images of hydrated cement paste, it appears that dosing cement samples with LN is not affecting the growth of ettringite or calcium silicate hydrate during cement hydration.

Fresh air content results of laboratory-mixed concrete showed that LN generally lowered the air content in air-entrained mixtures. The results of air content testing of field-mixed concrete showed that air-entrained concrete experienced a negligible reduction in air content after LN dosing in all four mixtures. In contrast, the non-air-entrained laboratory concrete mixtures did not show the same loss of air as did the air-entrained mixtures.

The hardened air content data showed that LN mixtures had less air content than control mixtures in 4 out of 5 cases, with the difference being statistically significant in three of these. The data from hardened air void testing also showed a loss of air content for in-place concrete as compared to fresh concrete and that LN does not affect the spacing factor of concrete. Results for specific surface measurements show that although there was an increase in the specific surface for some mixtures, it appears that the increase is a function of the decreasing air content rather than increasing bubble surface area.

Results of a metallurgical analysis performed on steel fragments that were taken from a mixing drum that had cracked due to LN dosing showed that the steel used to

fabricate the mixing drums was most likely manufactured with scrap metal with a high carbon content. This makes the mixing drums very susceptible to brittle failure. Cracking typically occurred towards the top of the mixing drum, in the vicinity where the LN lance is inserted into the drum. Crack propagation followed no distinct path, indicating that cracking is most likely not a thermal fatigue issue but rather a brittle fracture that propagates at high velocities. It is hypothesized that cracking may be caused by misaligned LN lances that spray onto the fins and the sides of the mixing drum.

Temperature data from iButton sensors showed temperatures in the mixing drum during one dosing application of -8.5°F and -15°F for the fin. It should be noted that the lance was aligned properly in this testing and temperatures could be much lower if misaligned. Concrete mixing drums will always be susceptible to cracking given the present quality of steel that is being used to fabricate the drums along with the sub-zero temperatures to which the mixing drums are being exposed.

Based on findings from this research study, liquid nitrogen is recommended as a primary cooling option to reduce the placement temperature of fresh concrete.

9.2 FUTURE WORK

Further testing should be conducted on delayed dosing mixtures. Research results show the possibility of extending transport times for ready-mix trucks as well as the possibility of batching concrete at separate locations and cooling the mixture at another location. Testing should investigate the relationship between delayed applications of LN, temperature, and setting time. Guidelines should be developed to specify cooling temperature, the time at which dosing should occur, and the length of time that initial set is prolonged.

A more detailed analysis should also be conducted to further investigate the effects of pre-heating on early-age cement hydration. Research results show that cement hydration is significantly affected by high temperatures if mixtures are not cooled within the first 5 seconds of cement and water contact. Research should focus on solution testing of early-age samples to monitor early-age hydration development.

Water loss testing showed that LN-cooled mixtures had increased strengths and decreased permeability as a result of water evaporation. Further testing should be conducted to determine the amount of water lost to evaporation during LN dosing. One way of doing this is to incrementally decrease the water-cement ratio of room temperature concrete mixtures and subsequently testing the compressive strength and permeability. These results should be matched to compressive strength and permeability data from LN-cooled concrete mixtures to determine the estimated water-cement ratio of concrete mixtures after LN application.

Lastly, future research should also investigate the cause of cracking in concrete mixing drums. Research should focus on steel quality and lance positioning. Guidelines should be developed to determine optimal steel compositions that are cost-effective and to suggest possible methods to ensure that LN injection lances are properly aligned.

APPENDIX A: Mortar Cube Compressive Strength

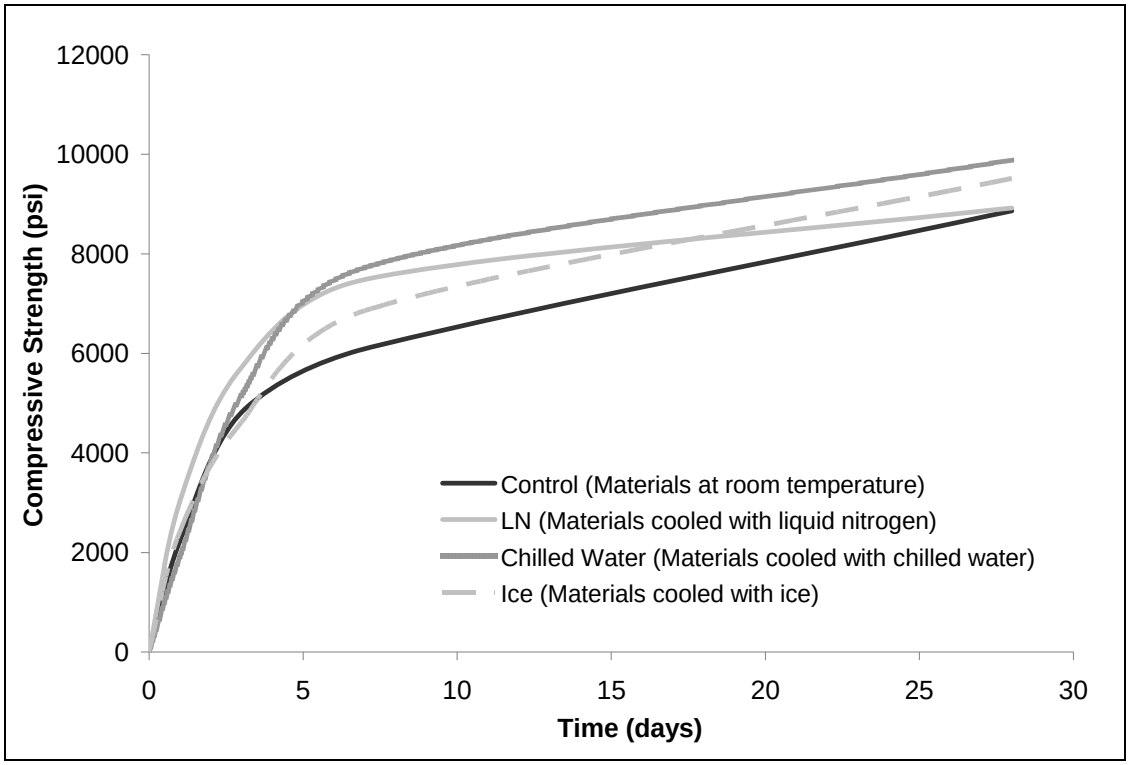


FIGURE A1 Compressive strength of replicated mortar cubes containing no admixtures

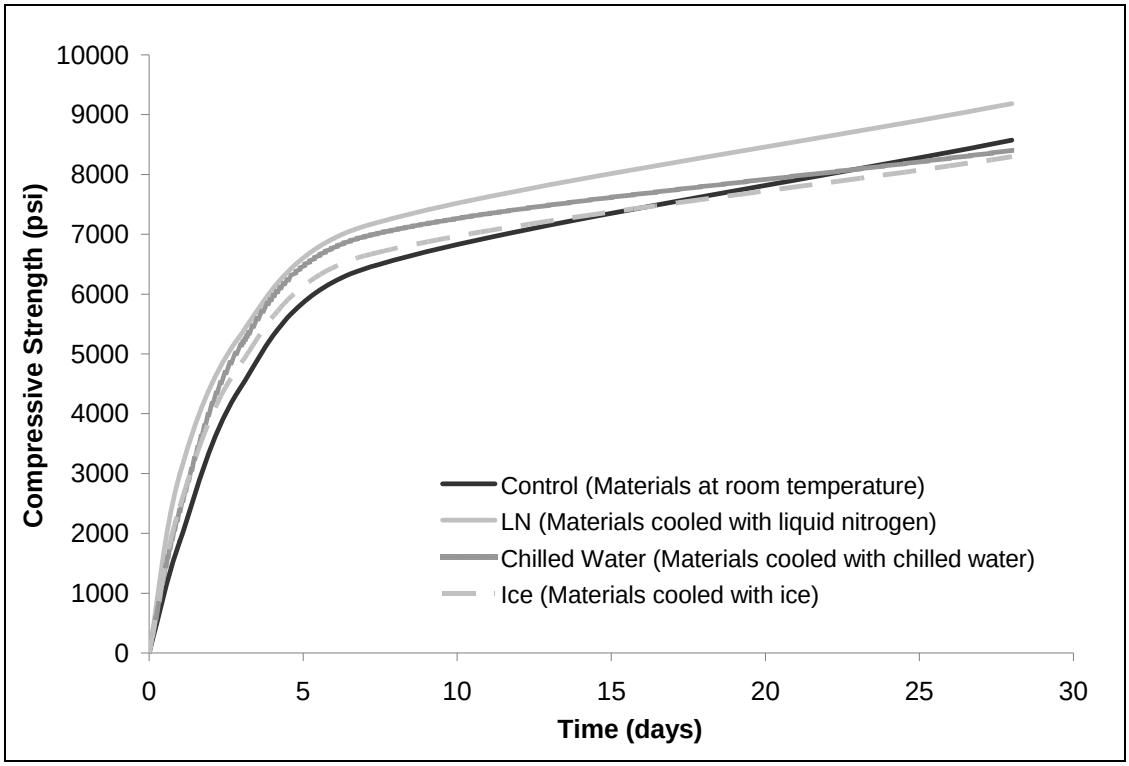


FIGURE A2 Compressive strength of replicated mortar cubes containing Rheobuild 1000

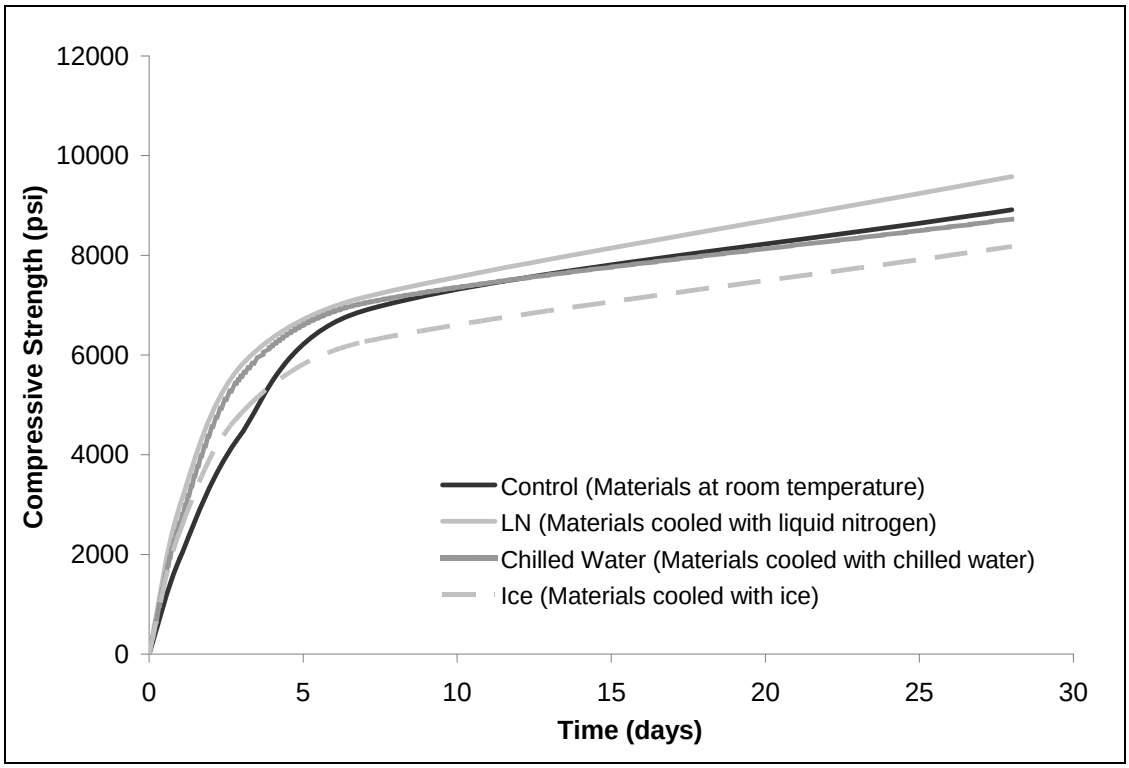


FIGURE A3 Compressive strength of replicated mortar cubes containing ADVA Flow

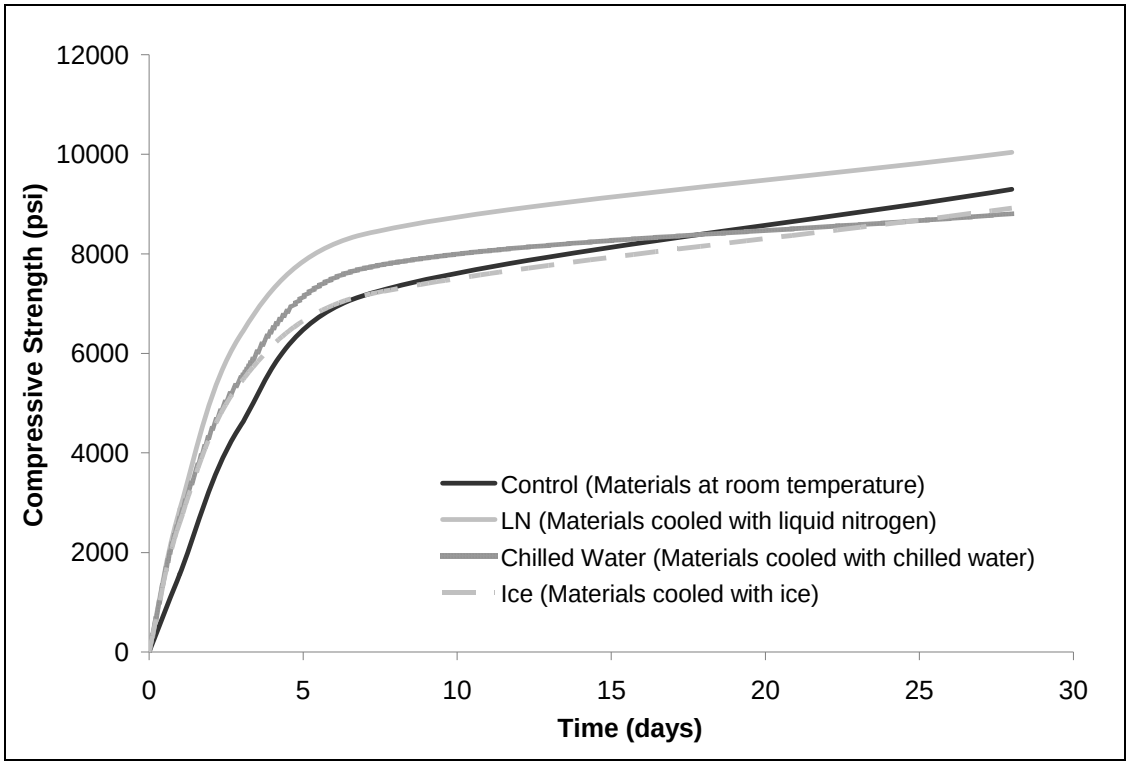


FIGURE A4 Compressive strength of replicated mortar cubes containing Pozzolith 961R

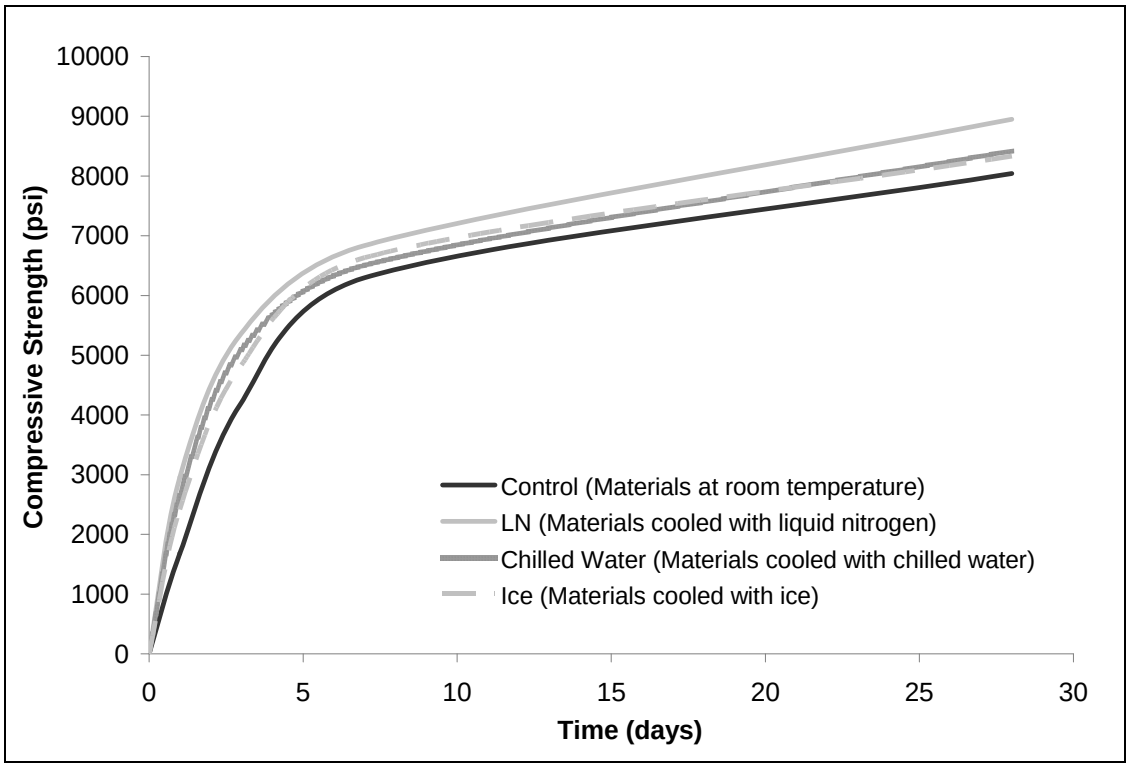


FIGURE A5 Compressive strength of replicated mortar cubes containing Pozzolith 200N

APPENDIX B: 1- and 7-day Compressive Strength Results for Laboratory-Mixed Concrete

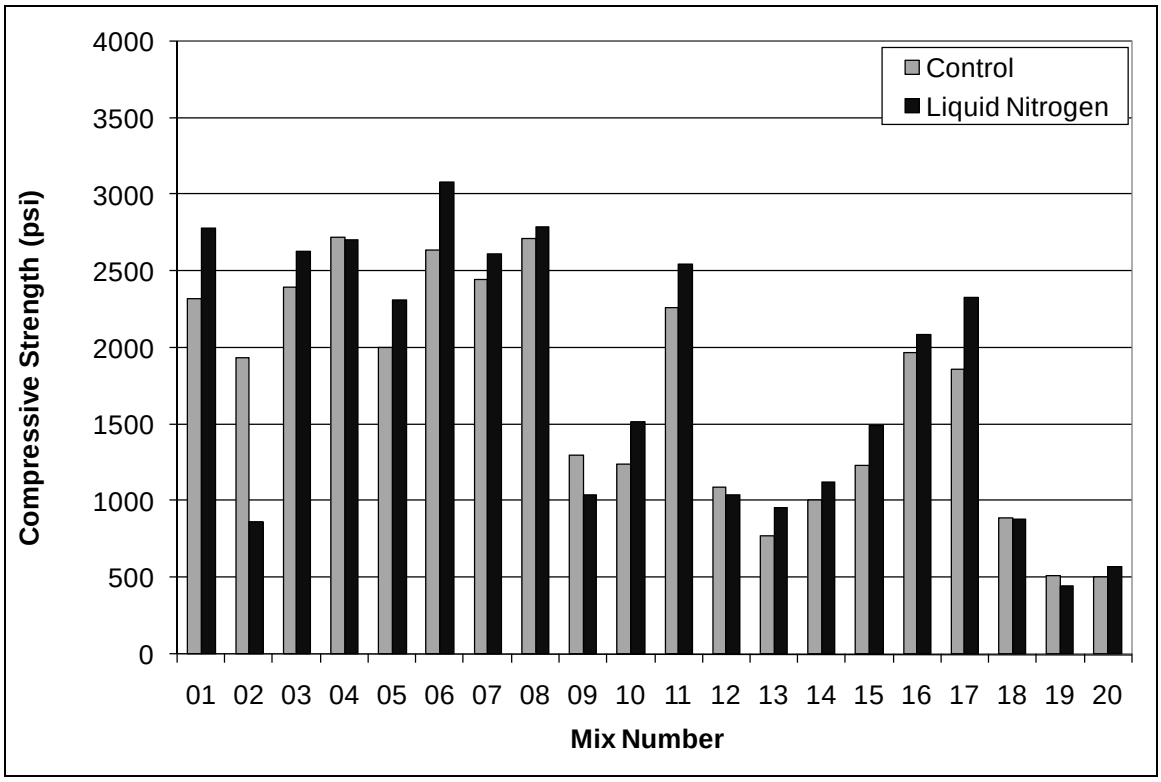


FIGURE B1 1-day compressive strengths for laboratory-mixed concrete

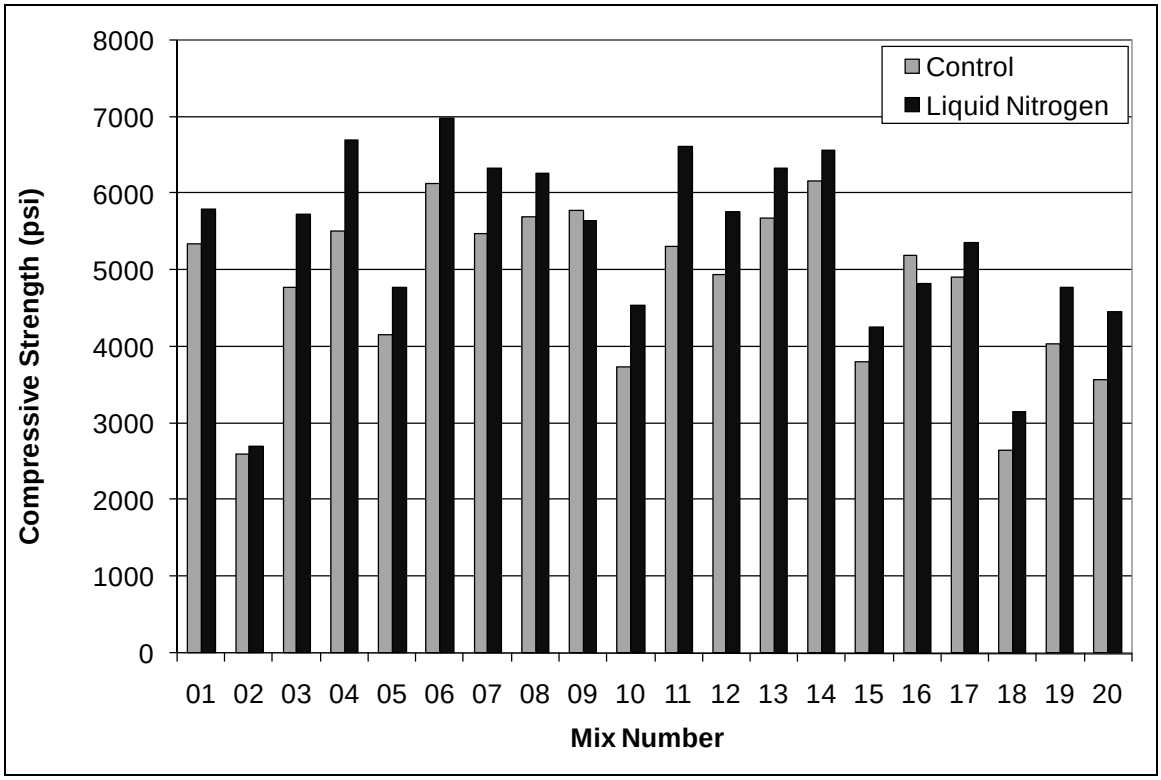


FIGURE B2 7-day compressive strengths for laboratory-mixed concrete

APPENDIX C: Semi-Adiabatic Calorimetry

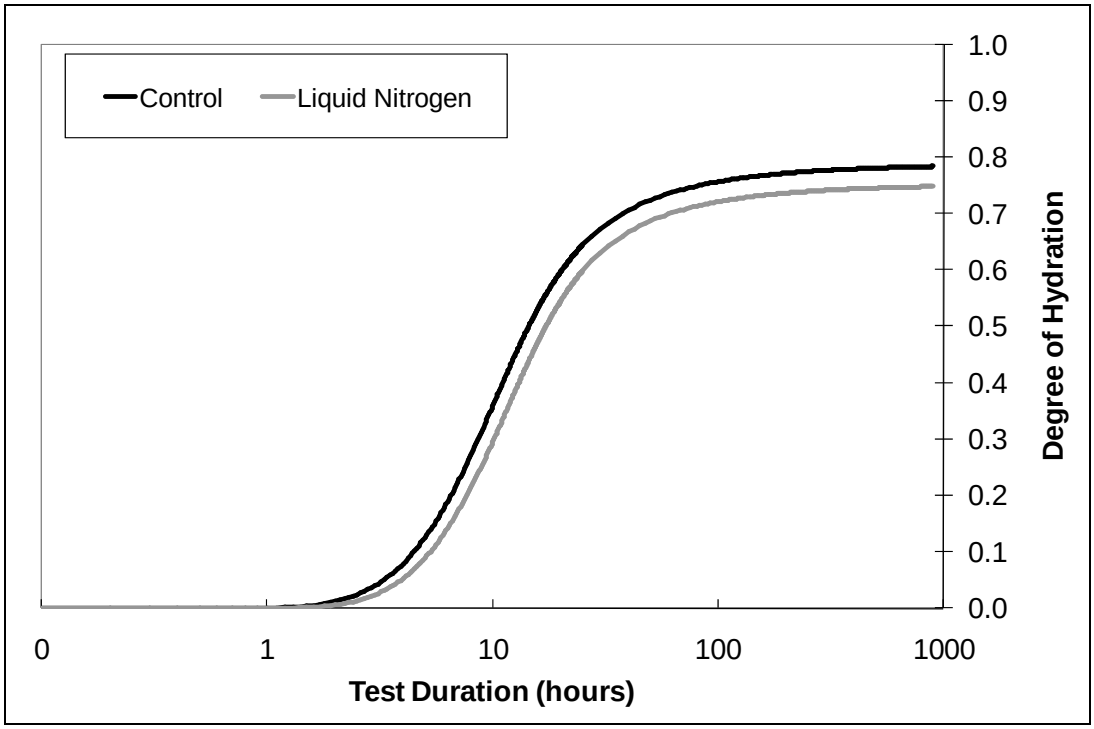


FIGURE C1 Degree of hydration curves from semi-adiabatic calorimetry for Mixture 1 (control)

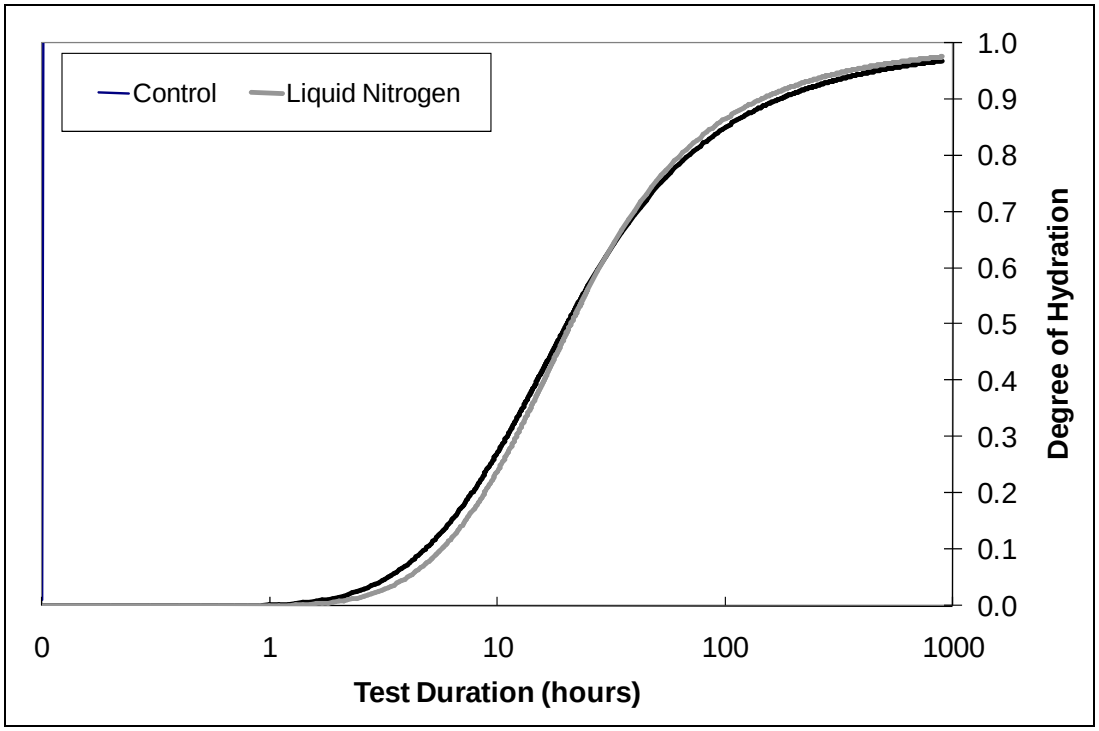


FIGURE C2 Degree of hydration curves from semi-adiabatic calorimetry for Mixture 2 (Class F fly ash)

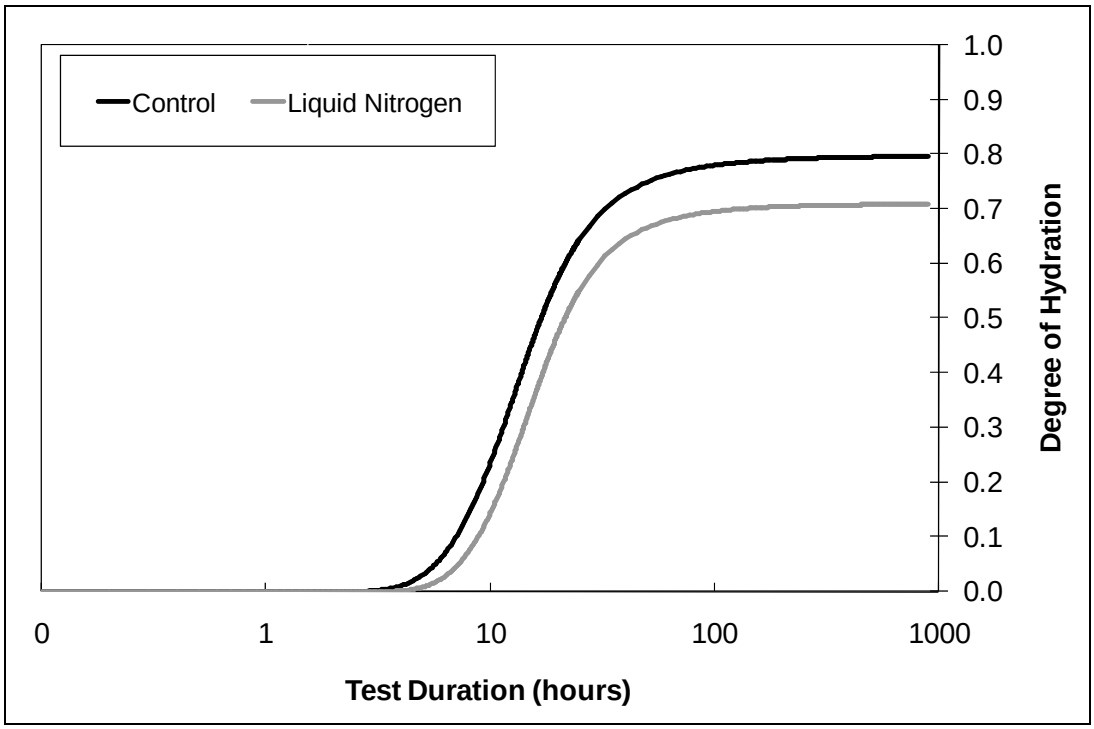


FIGURE C3 Degree of hydration curves from semi-adiabatic calorimetry for Mixture 3 (low range water reducer)

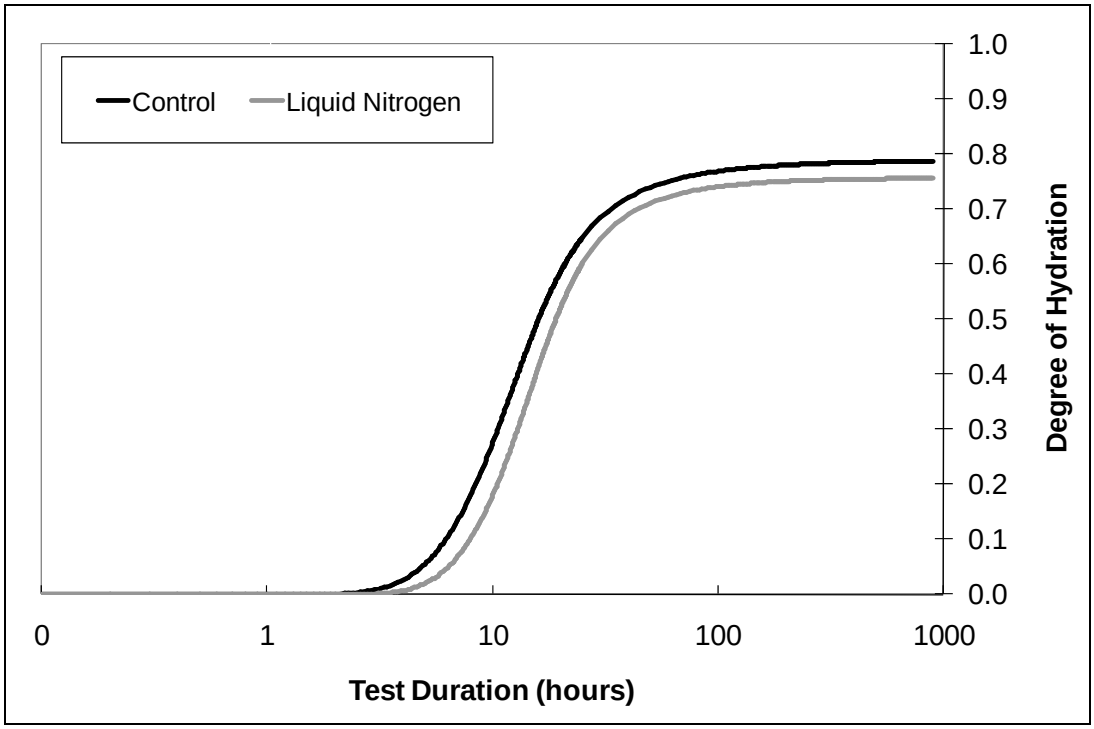


FIGURE C4 Degree of hydration curves from semi-adiabatic calorimetry for Mixture 4 (water reducer/retarder)

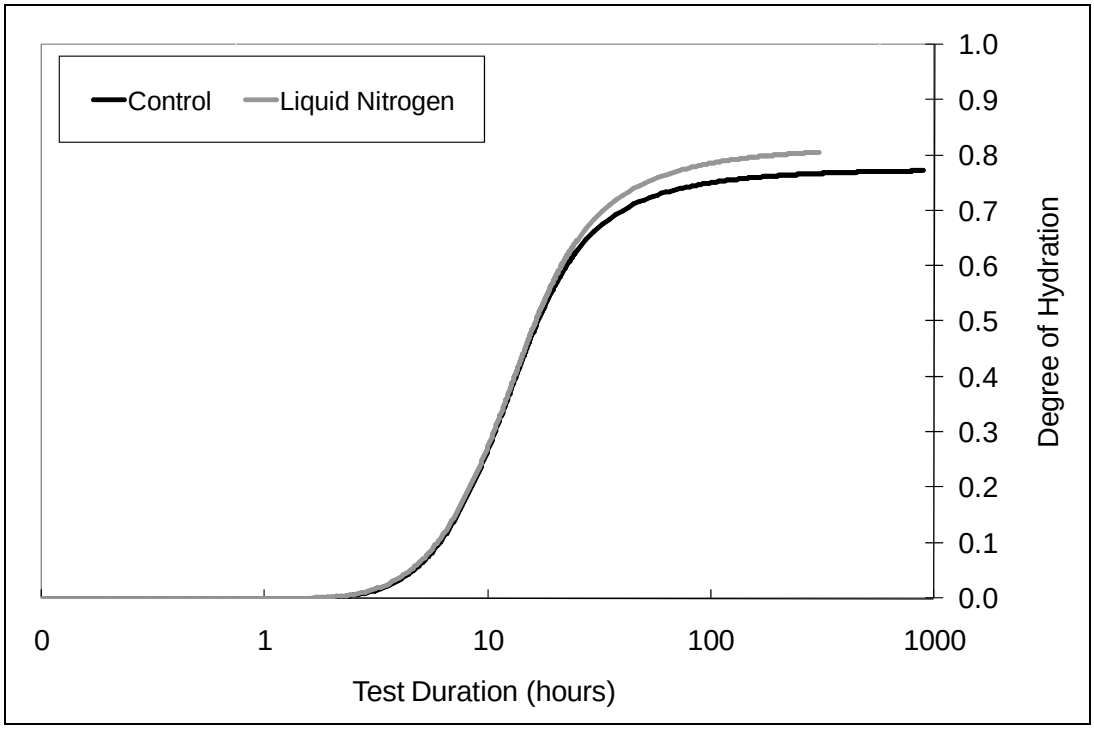


FIGURE C5 Degree of hydration curves from semi-adiabatic calorimetry for Mixture 5 (midrange water reducer)

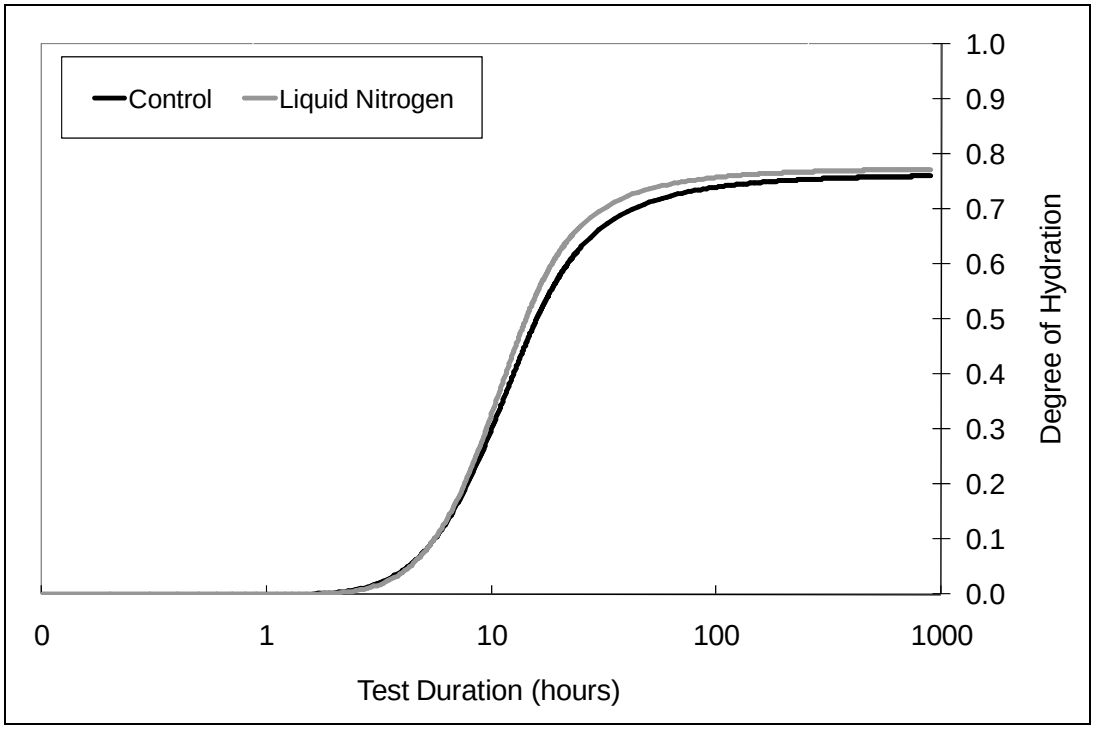


FIGURE C6 Degree of hydration curves from semi-adiabatic calorimetry for Mixture 6 (polycarboxylate superplasticizer)

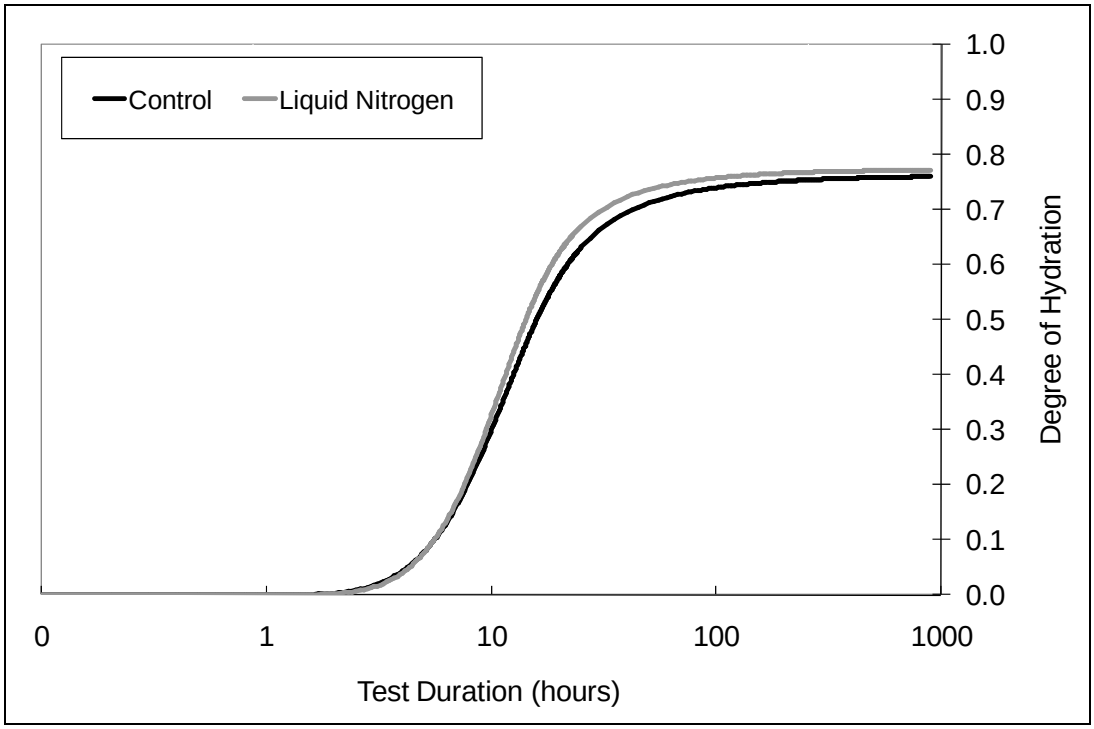


FIGURE C7 Degree of hydration curves from semi-adiabatic calorimetry for Mixture 7 (naphthalene superplasticizer)

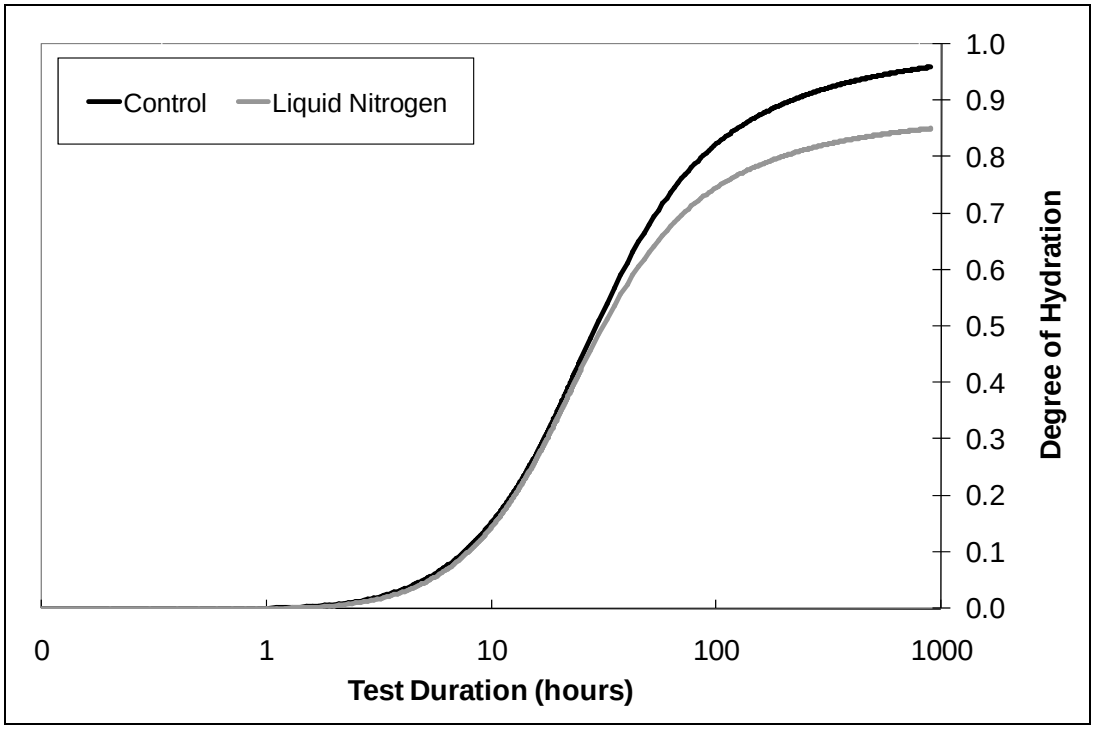


FIGURE C8 Degree of hydration curves from semi-adiabatic calorimetry for Mixture 9 (slag + polycarboxylate superplasticizer)

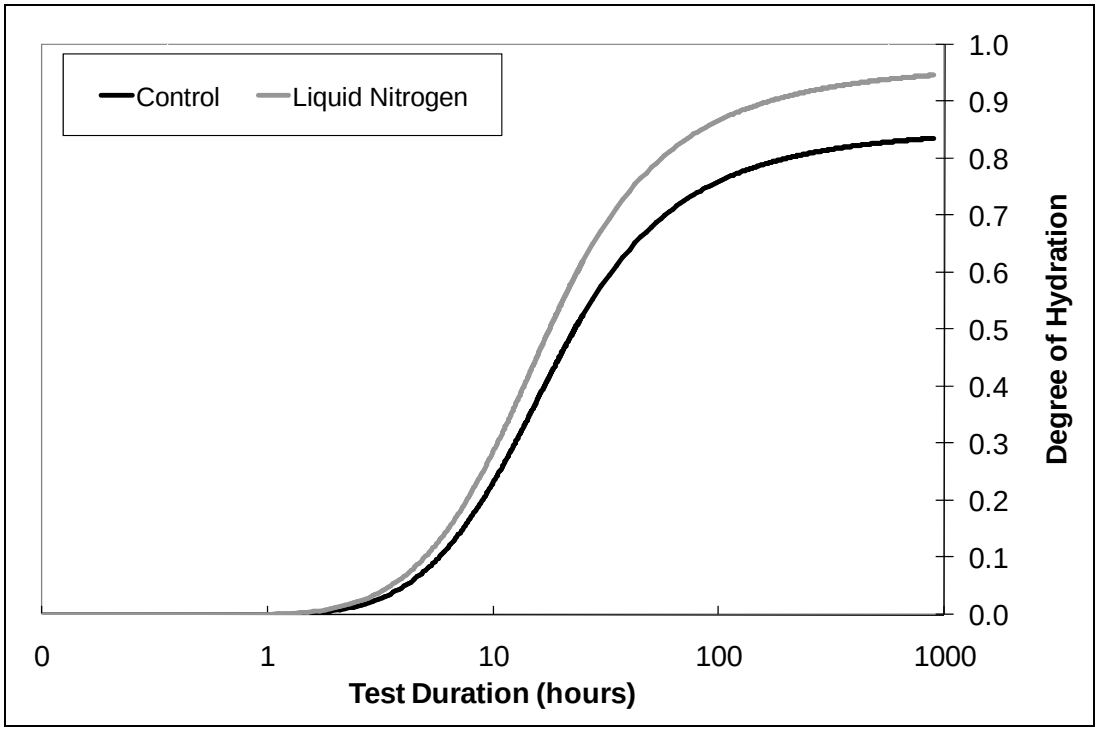


FIGURE C9 Degree of hydration curves from semi-adiabatic calorimetry for Mixture 10 (Class F fly ash + polycarboxylate superplasticizer)

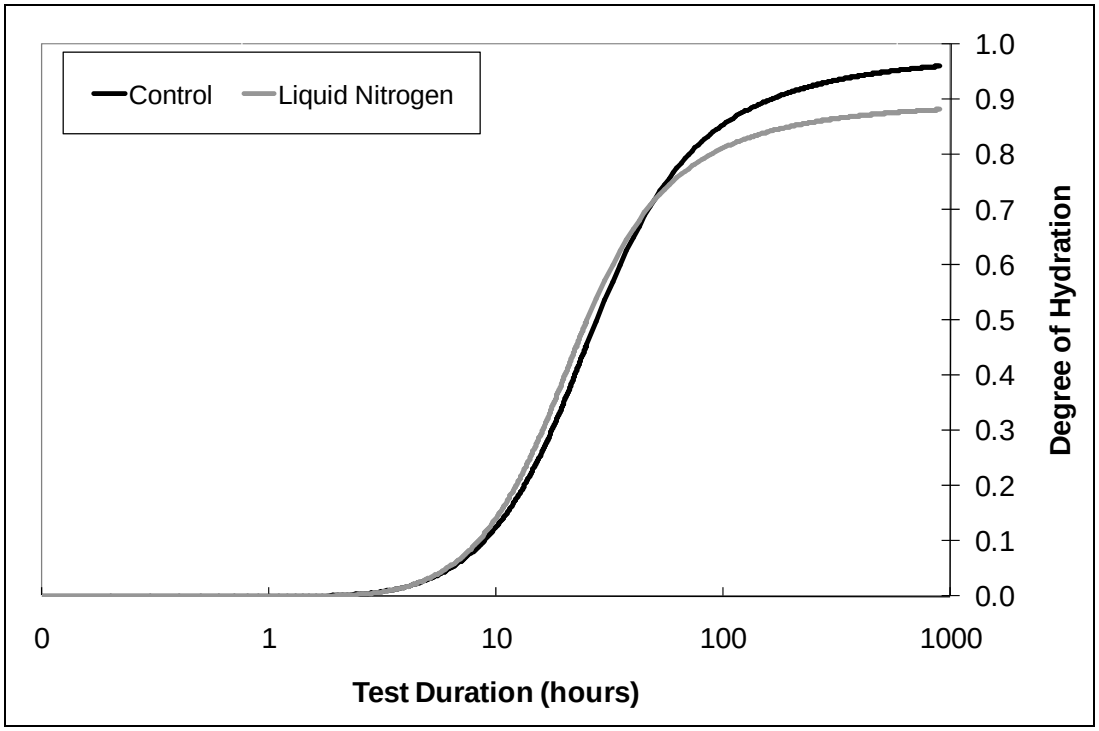


FIGURE C10 Degree of hydration curves from semi-adiabatic calorimetry for Mixture 13 (Class C fly ash + polycarboxylate superplasticizer)

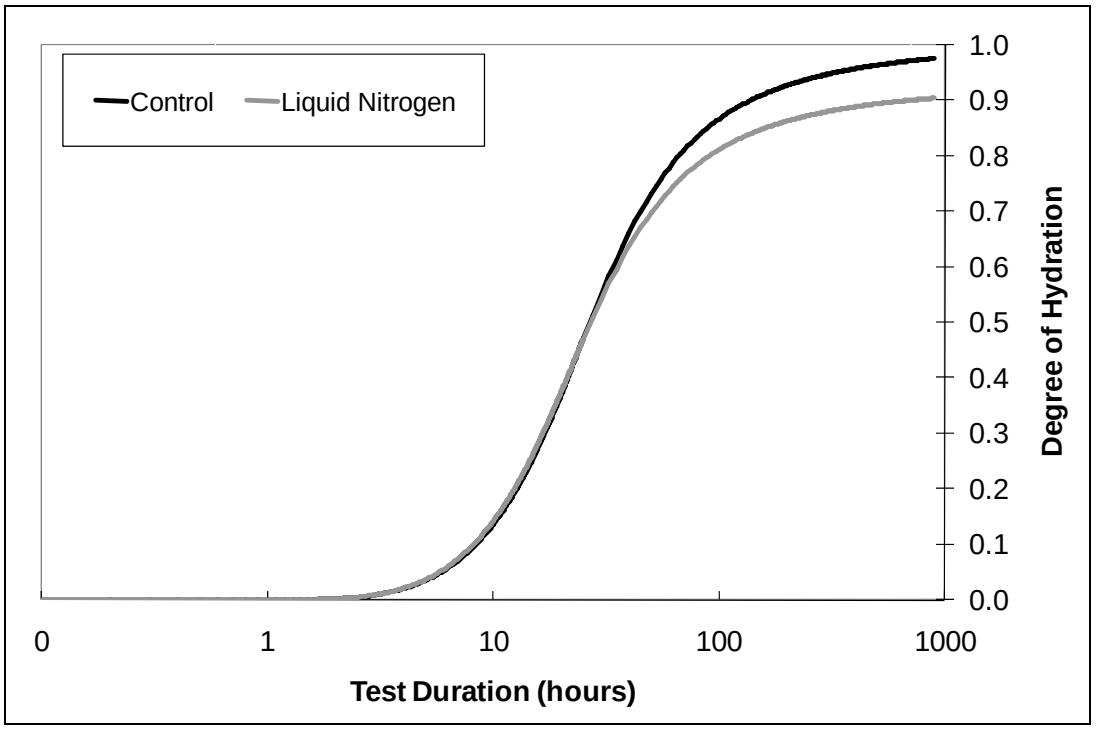


FIGURE C11 Degree of hydration curves from semi-adiabatic calorimetry for Mixture 14 (Class C fly ash)

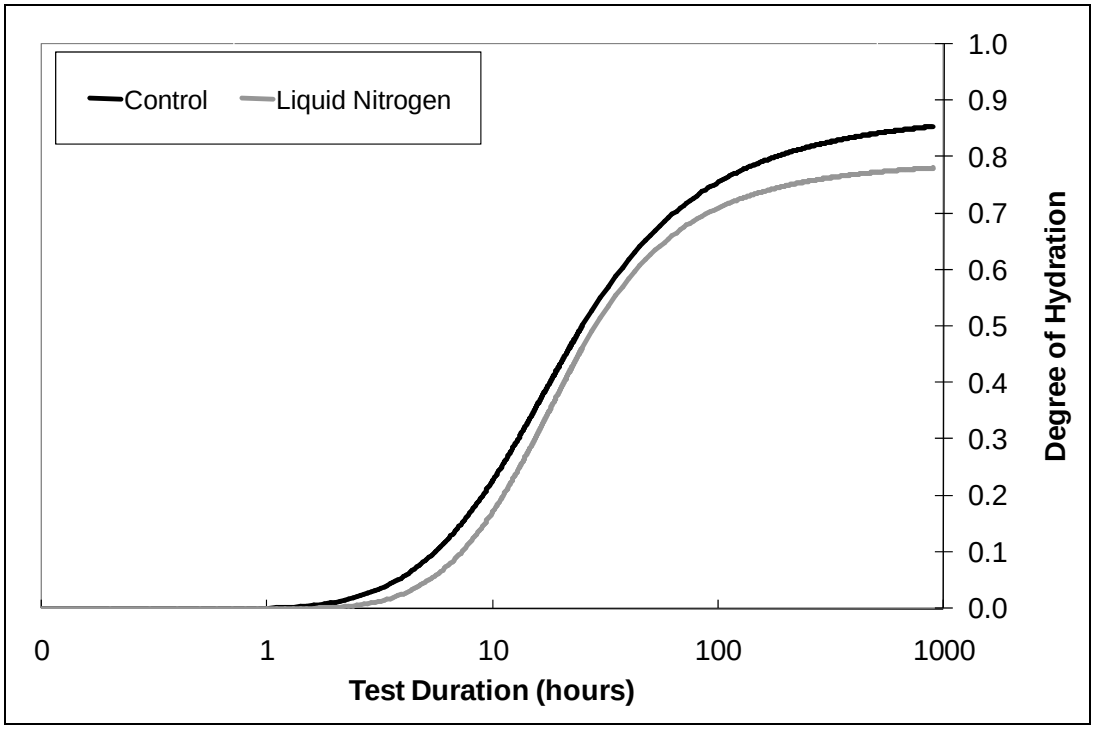


FIGURE C12 Degree of hydration curves from semi-adiabatic calorimetry for Mixture 18 (Class F fly ash + polycarboxylate superplasticizer + air entrainer)

APPENDIX D: Isothermal Calorimetry

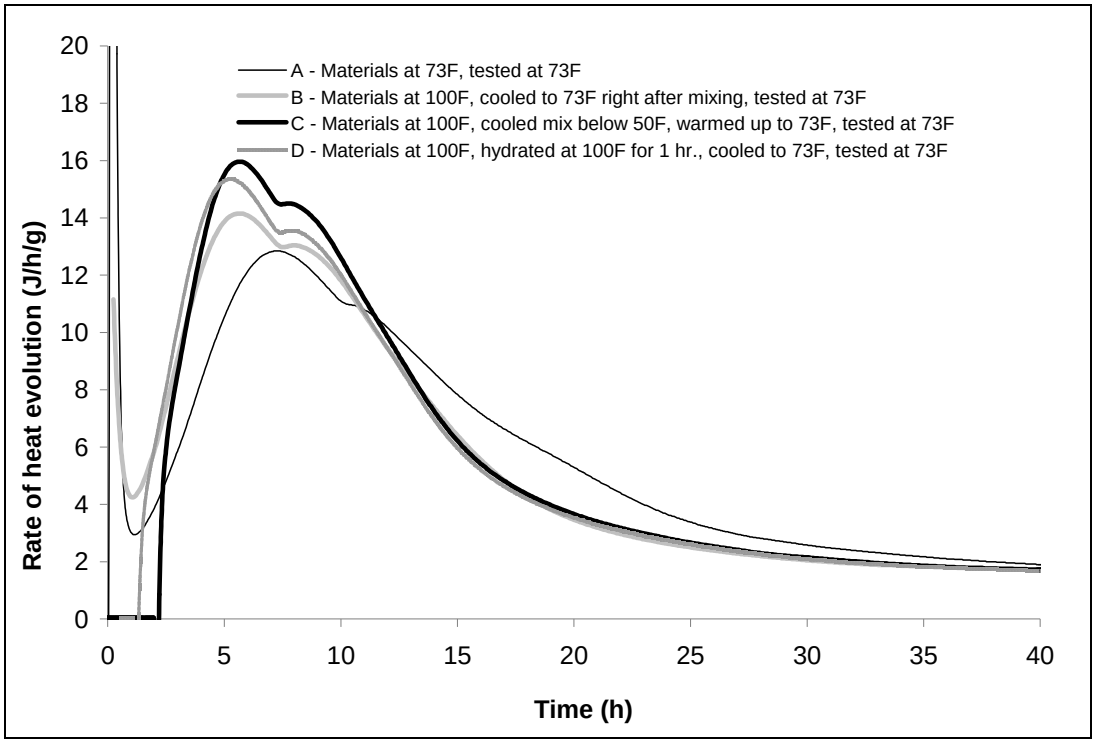


FIGURE D1 Rate of heat evolution curves for isothermal calorimetry Mixture 1 (control)

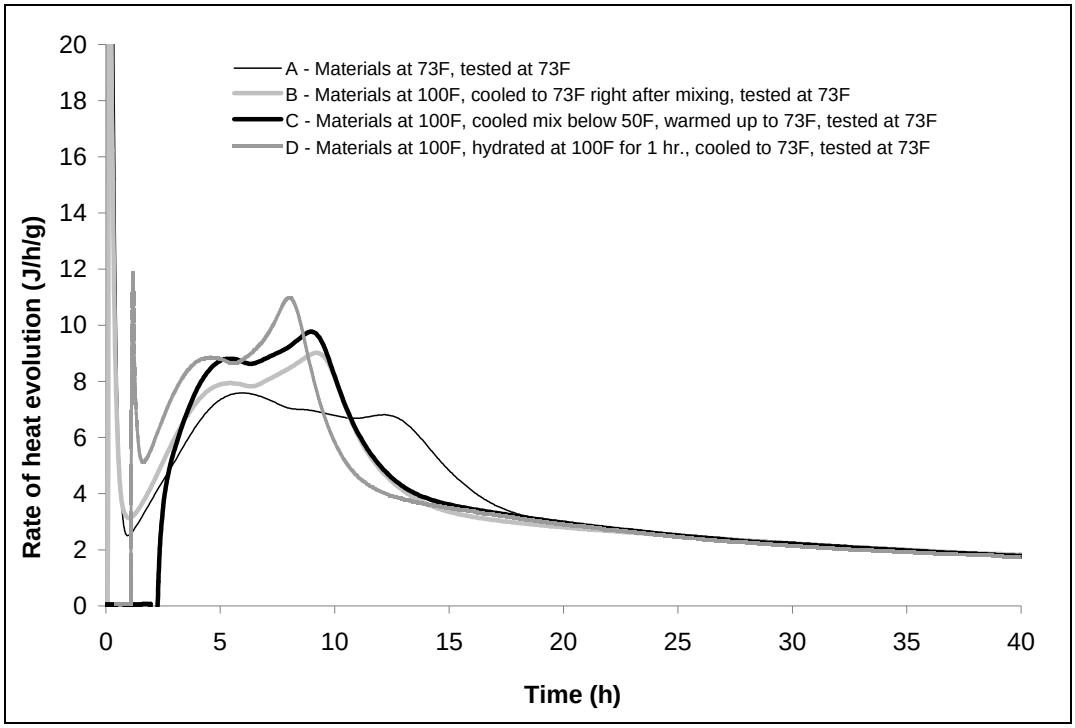


FIGURE D2 Rate of heat evolution curves for isothermal calorimetry Mixture 2 (slag-50%)

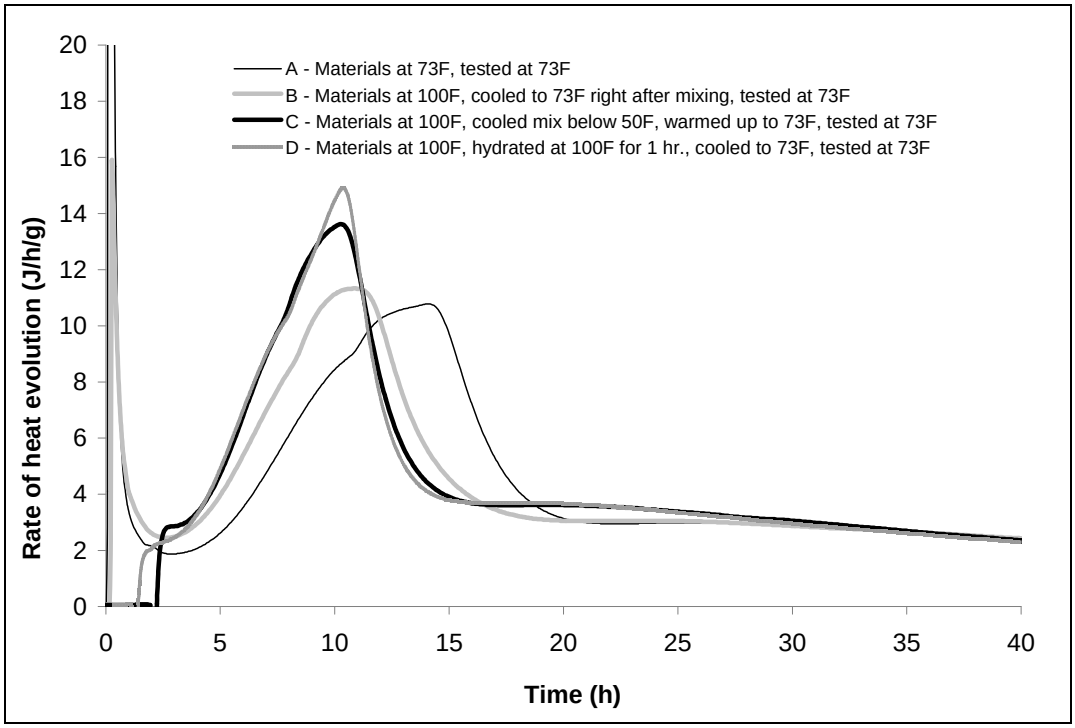


FIGURE D3 Rate of heat evolution curves for isothermal calorimetry Mixture 3 (30% C ash, Deely)

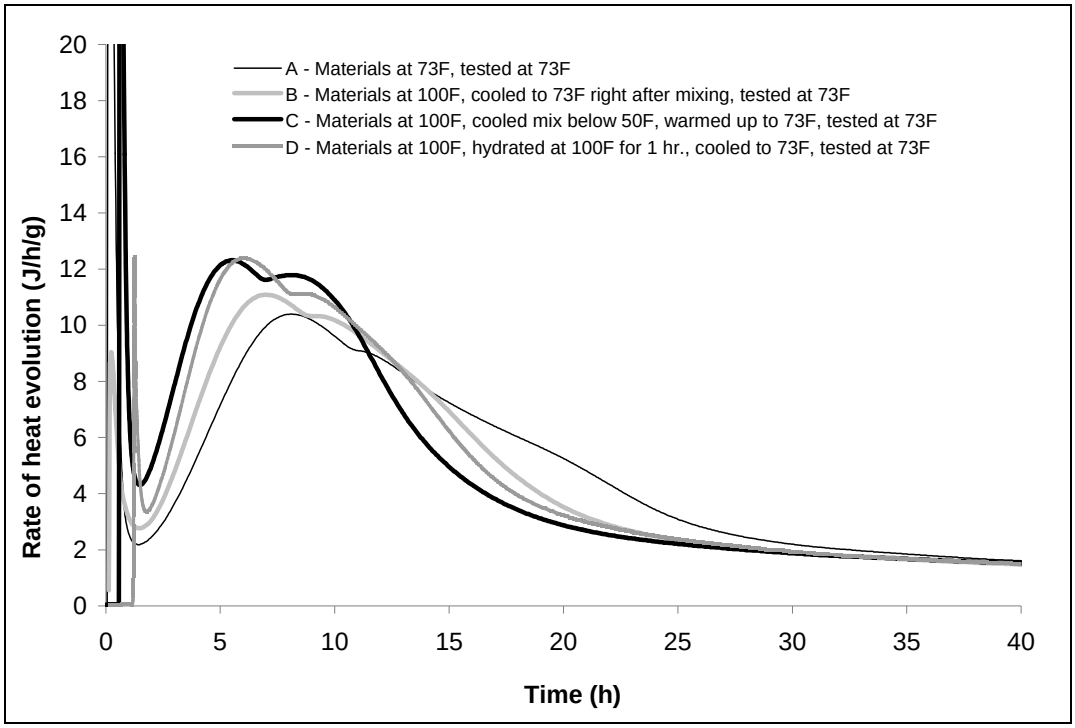


FIGURE D4 Rate of heat evolution curves for isothermal calorimetry Mixture 5 (20% F ash, Big Brown)

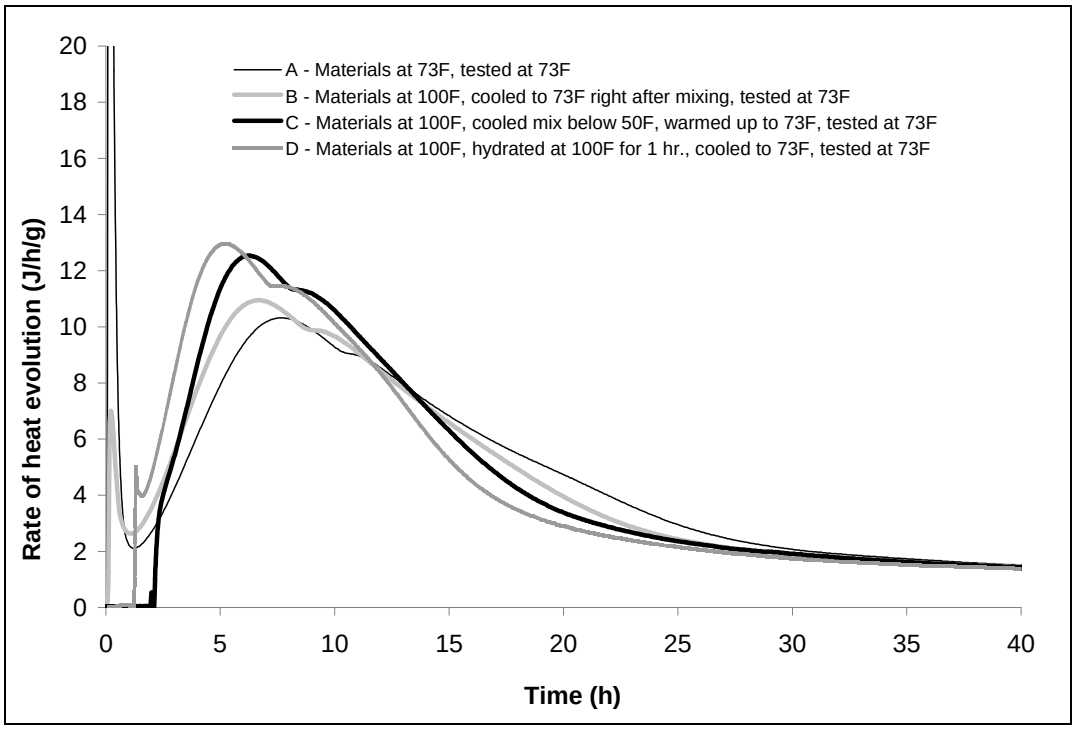


FIGURE D5 Rate of heat evolution curves for isothermal calorimetry Mixture 6 (20% F ash, Martin Lake)

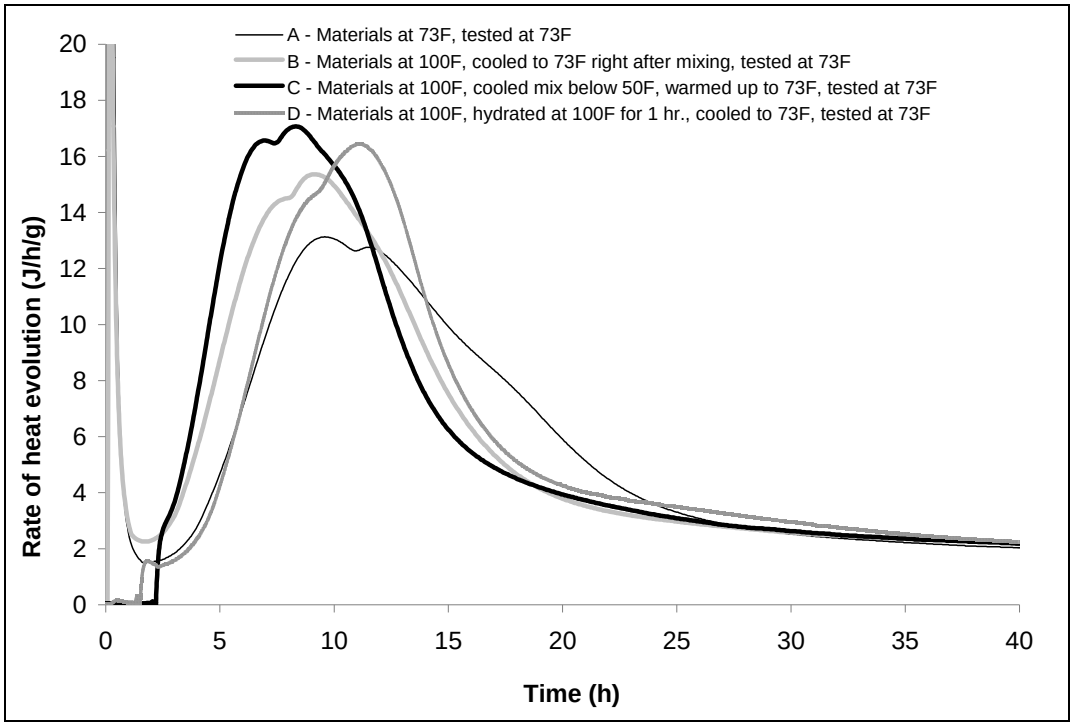


FIGURE D6 Rate of heat evolution curves for isothermal calorimetry Mixture 7 (Water reducer, MR)

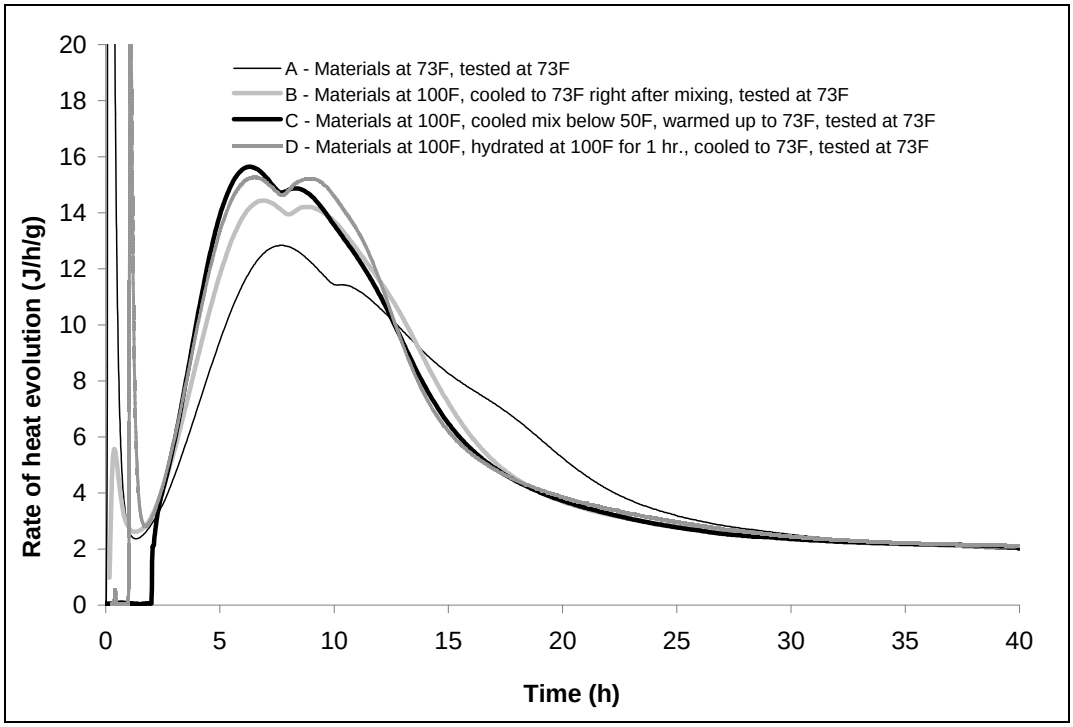


FIGURE D7 Rate of heat evolution curves for isothermal calorimetry Mixture 8 (Midrange water reducer, MRWR)

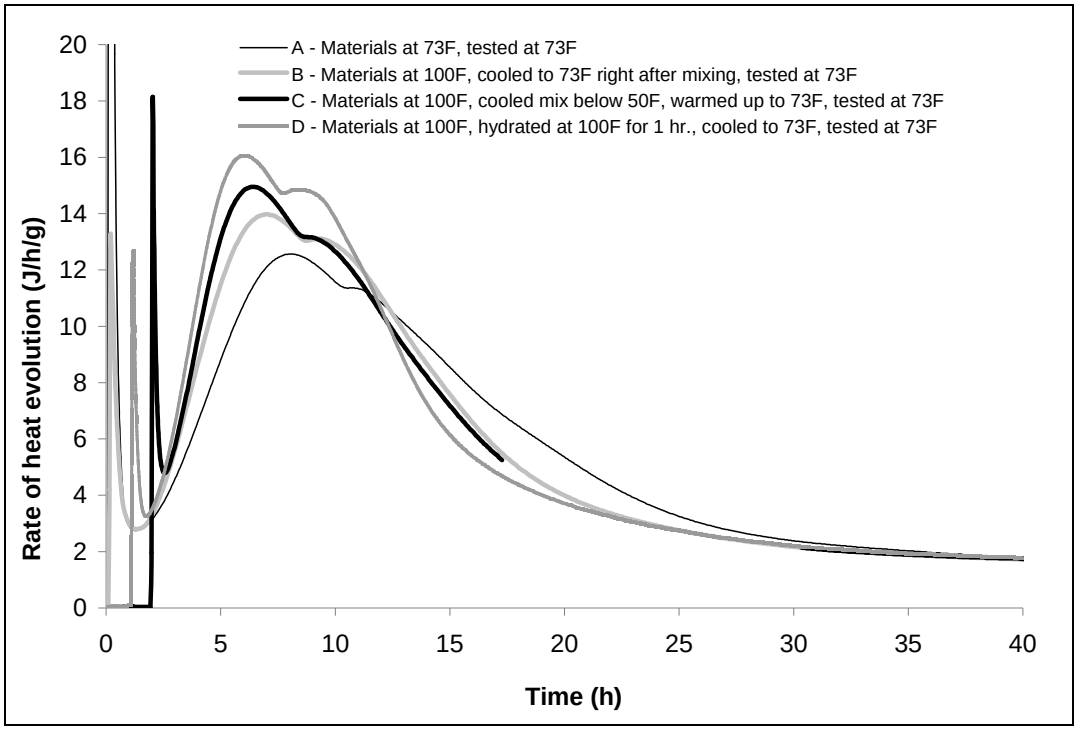


FIGURE D8 Rate of heat evolution curves for isothermal calorimetry Mixture 9 (Naphthalene superplasticizer, Naph)

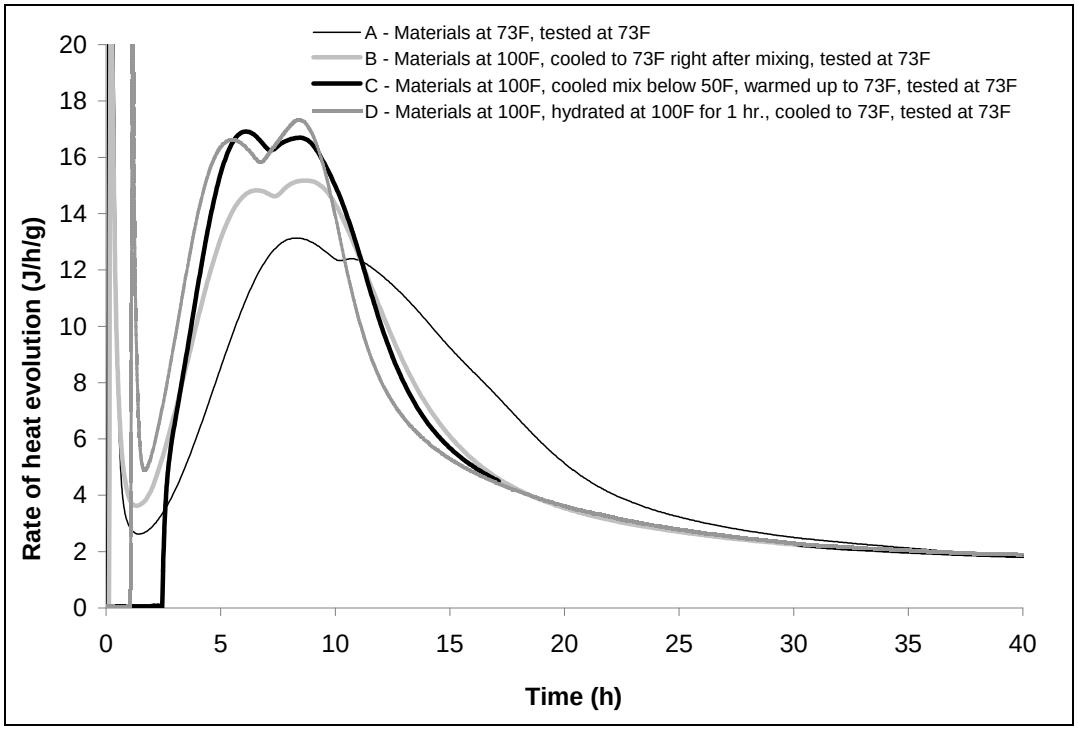


FIGURE D9 Rate of heat evolution curves for isothermal calorimetry Mixture 10 (Polycarboxylate superplasticizer)

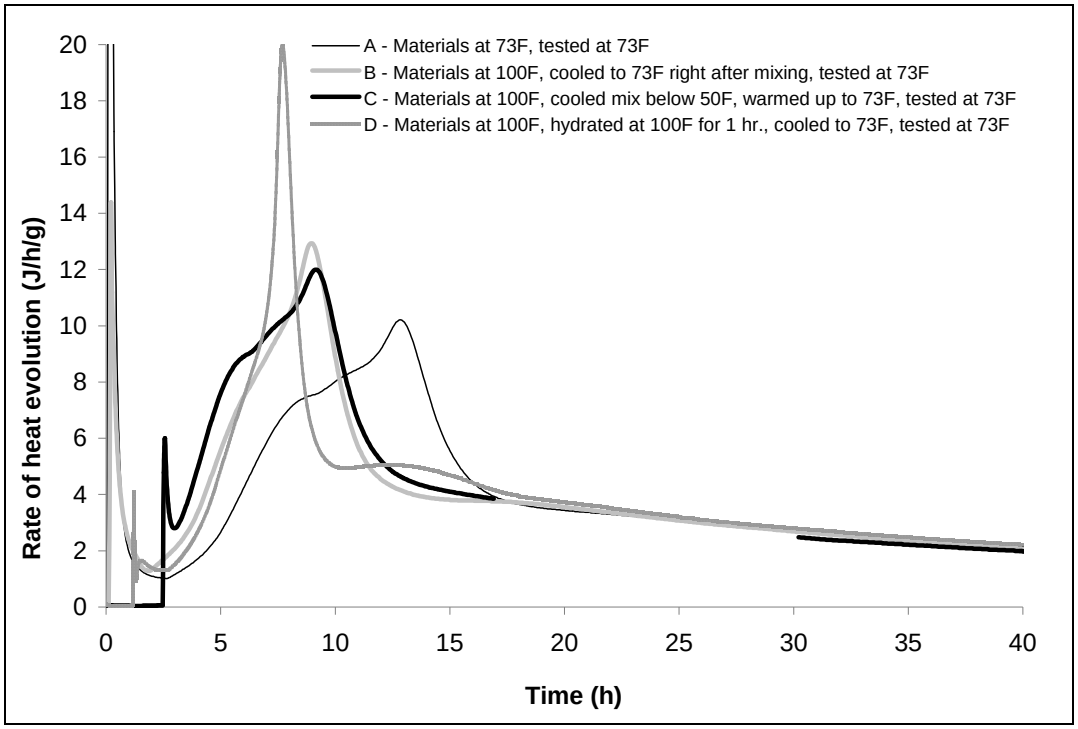


FIGURE D10 Rate of heat evolution curves for isothermal calorimetry Mixture 11 (Slag + WR)

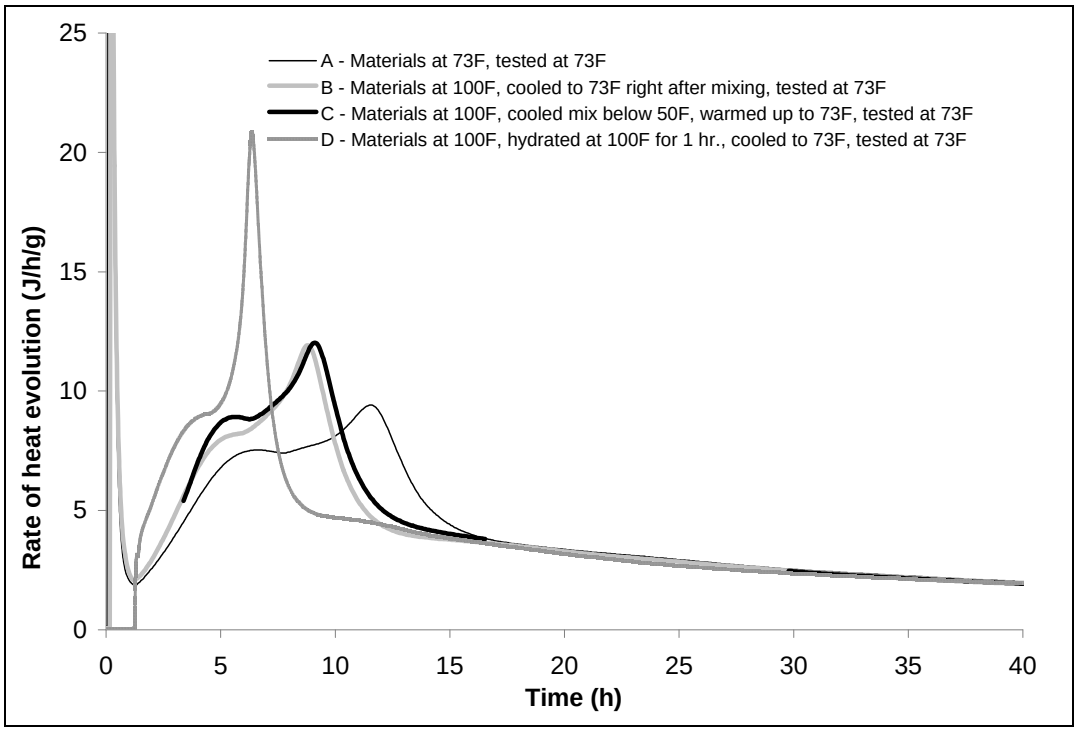


FIGURE D11 Rate of heat evolution curves for isothermal calorimetry Mixture 12 (Slag + MRWR)

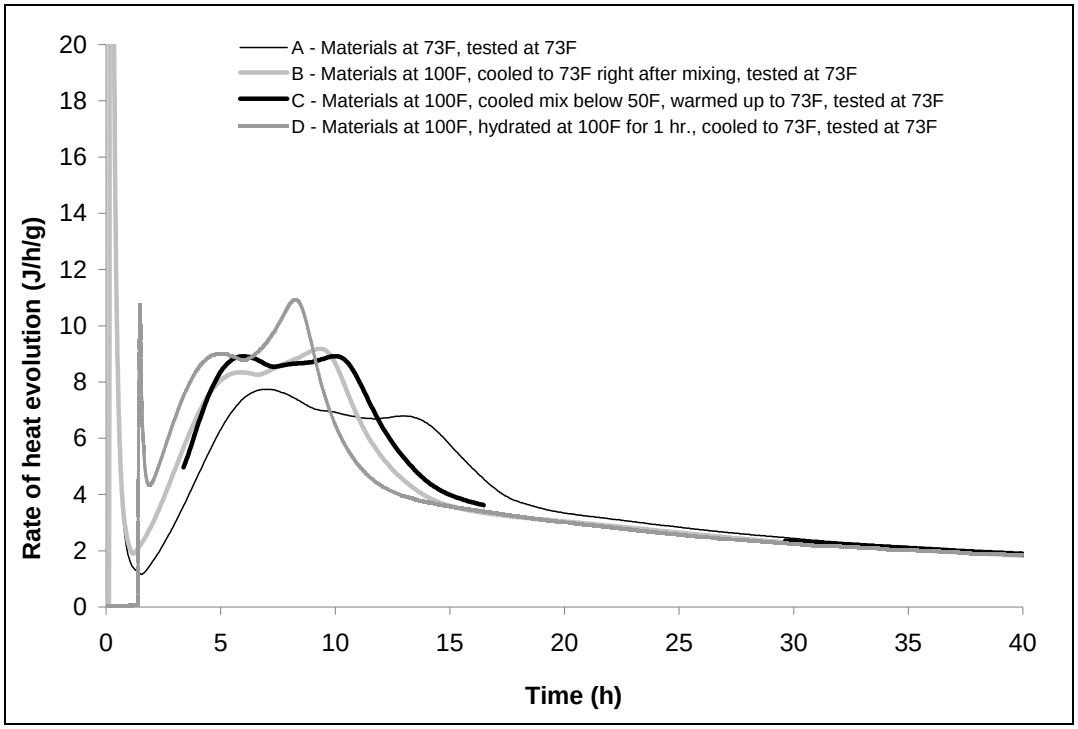


FIGURE D12 Rate of heat evolution curves for isothermal calorimetry Mixture 13 (Slag + Naph)

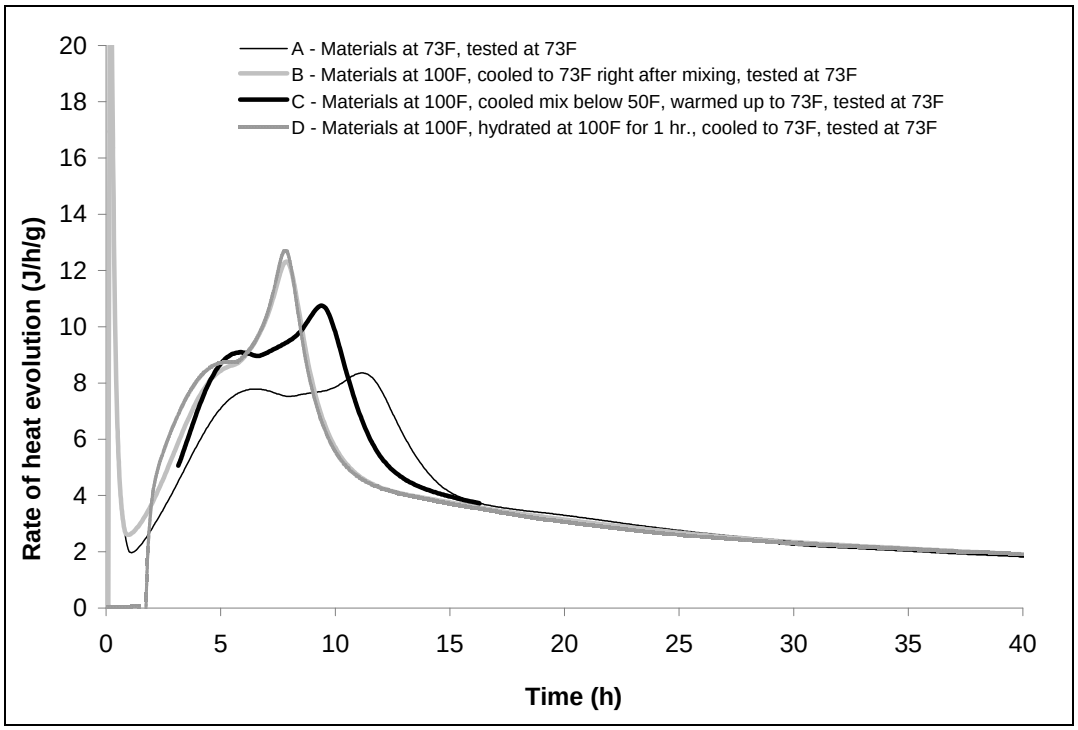


FIGURE D13 Rate of heat evolution curves for isothermal calorimetry Mixture 14 (Slag + Poly)

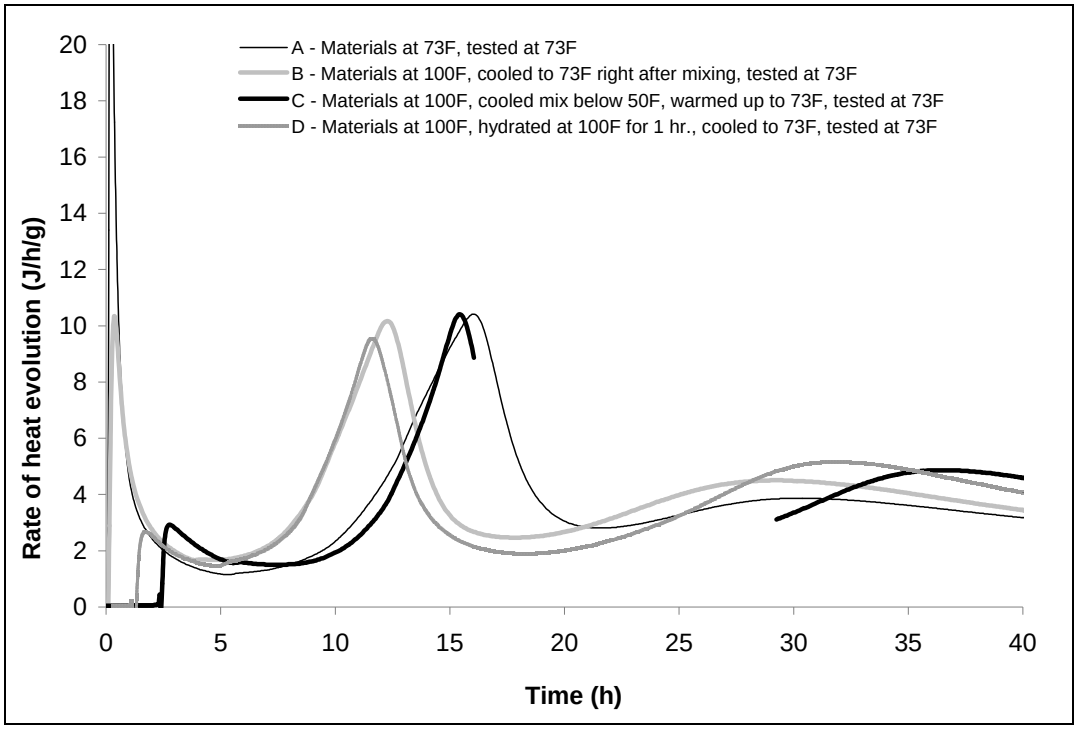


FIGURE D14 Rate of heat evolution curves for isothermal calorimetry Mixture 15 (C ash Deely + WR)

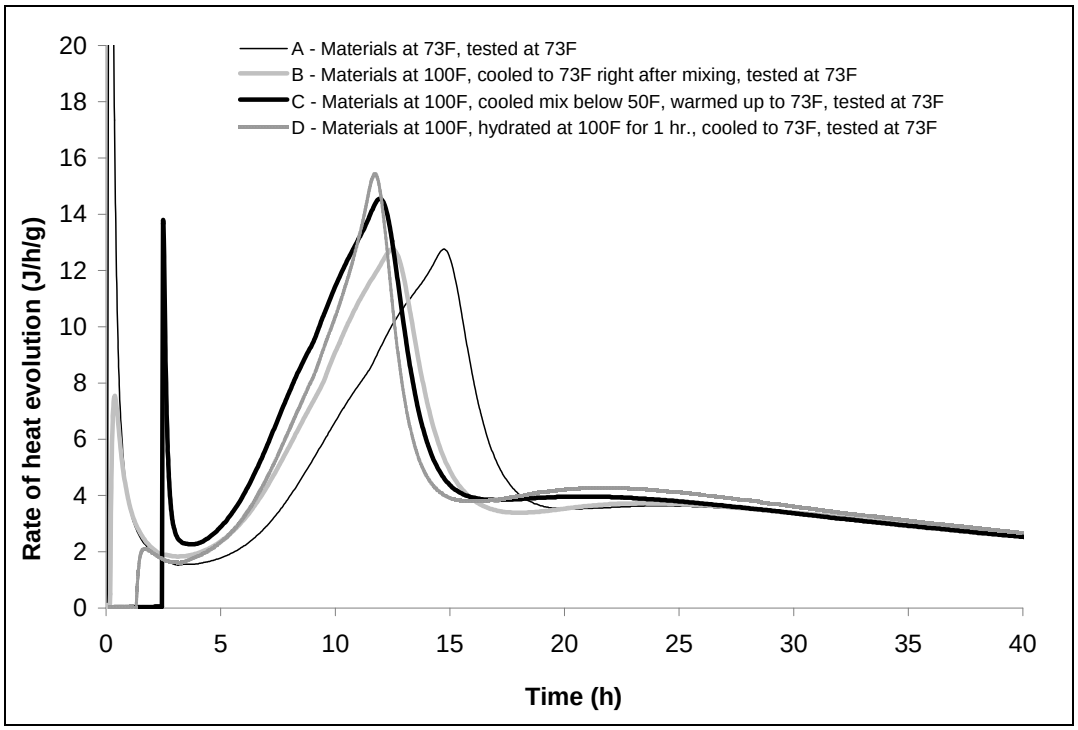


FIGURE D15 Rate of heat evolution curves for isothermal calorimetry Mixture 16 (C ash Deely + MRWR)

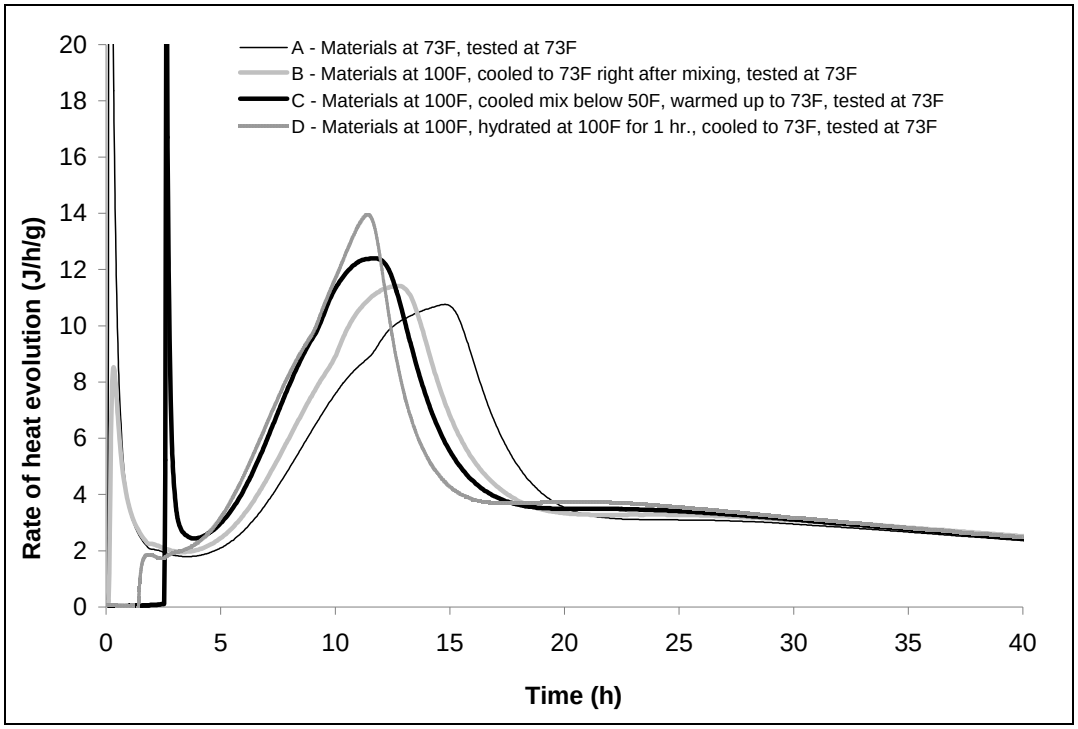


FIGURE D16 Rate of heat evolution curves for isothermal calorimetry Mixture 17 (C ash Deely + Naph)

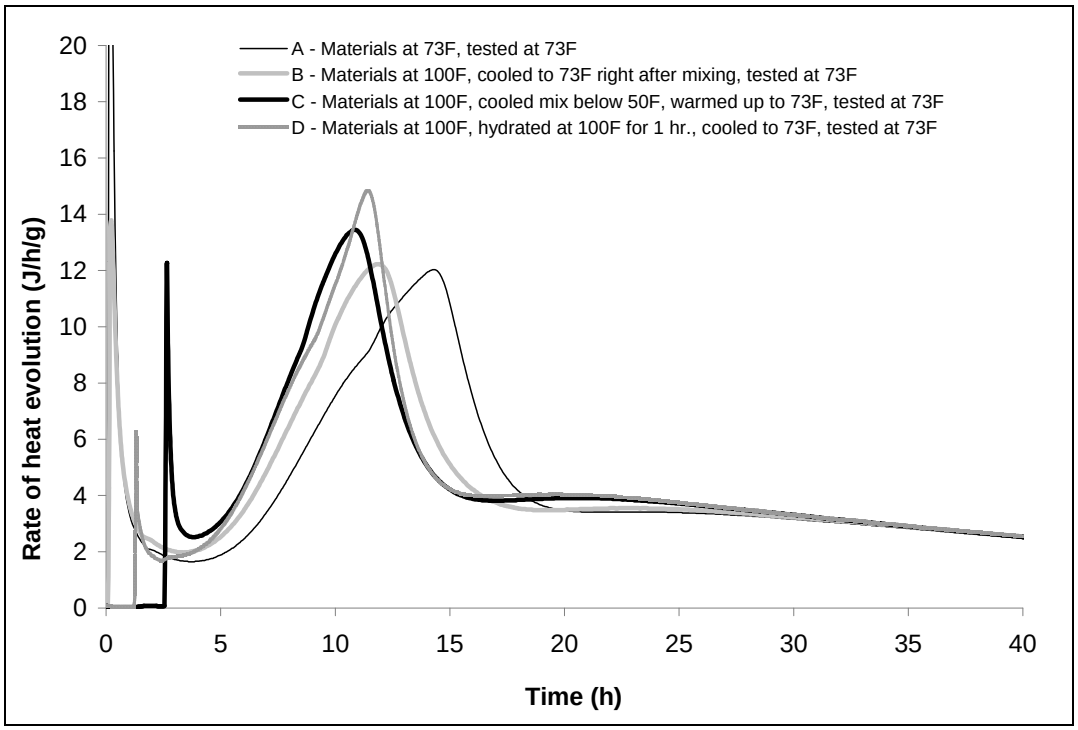


FIGURE D17 Rate of heat evolution curves for isothermal calorimetry Mixture 18 (C ash Deely + Poly)

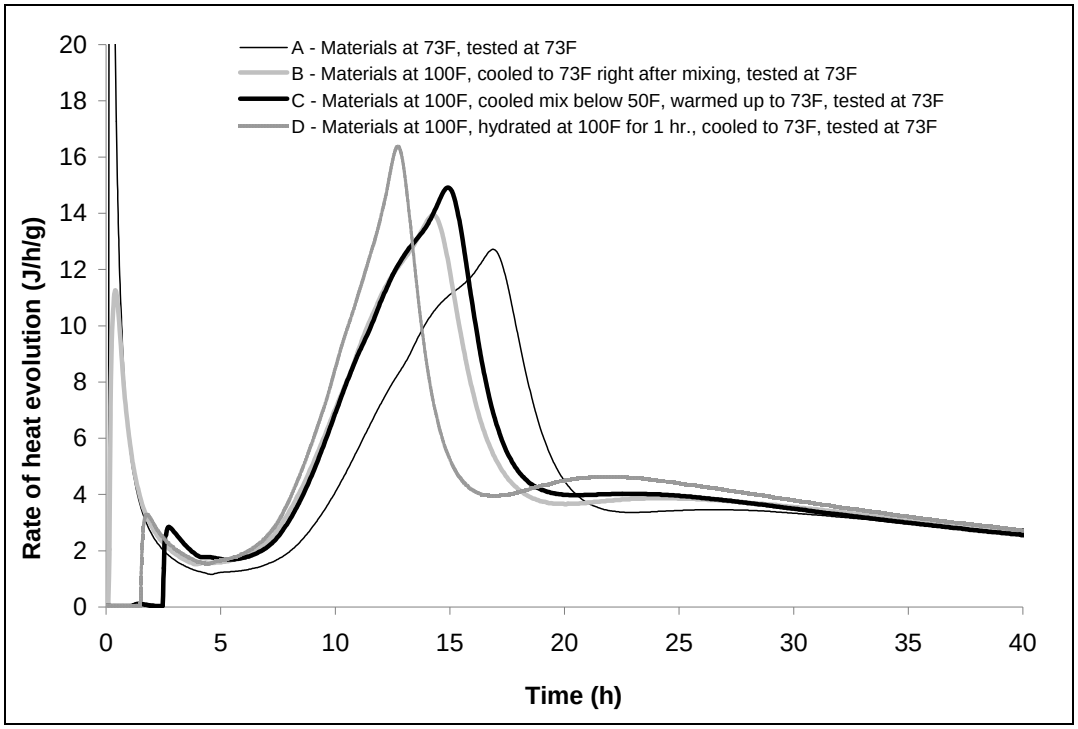


FIGURE D18 Rate of heat evolution curves for isothermal calorimetry Mixture 19 (C ash Parish + WR)

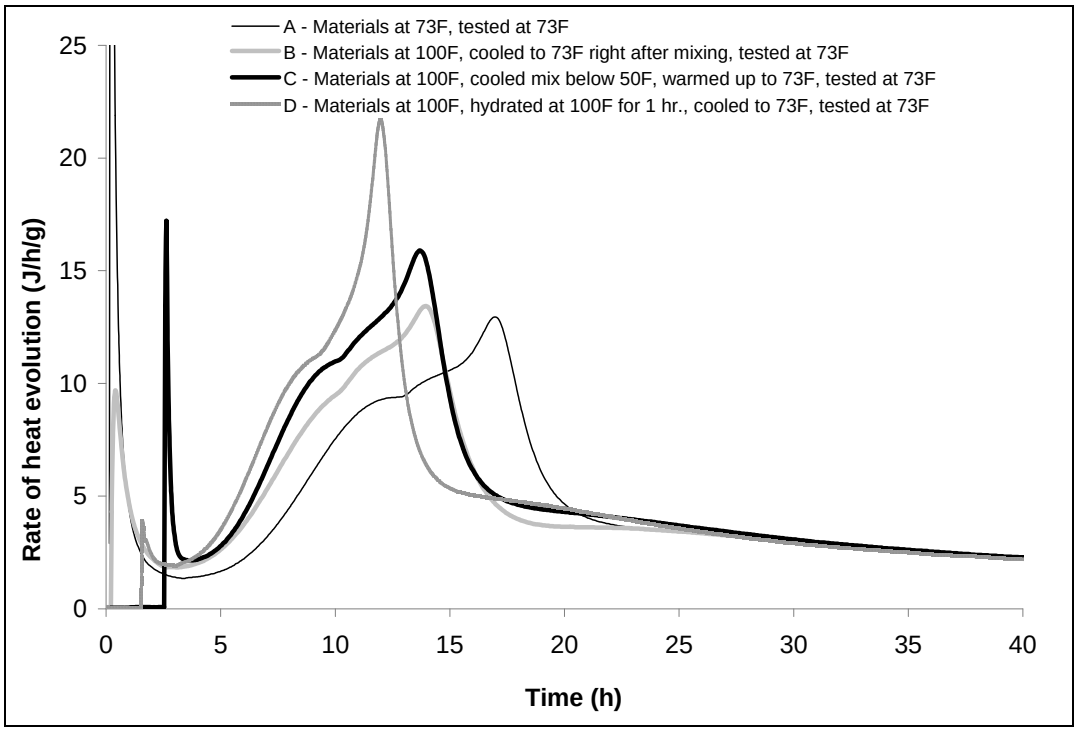


FIGURE D19 Rate of heat evolution curves for isothermal calorimetry Mixture 20 (C ash Parish + MRWR)

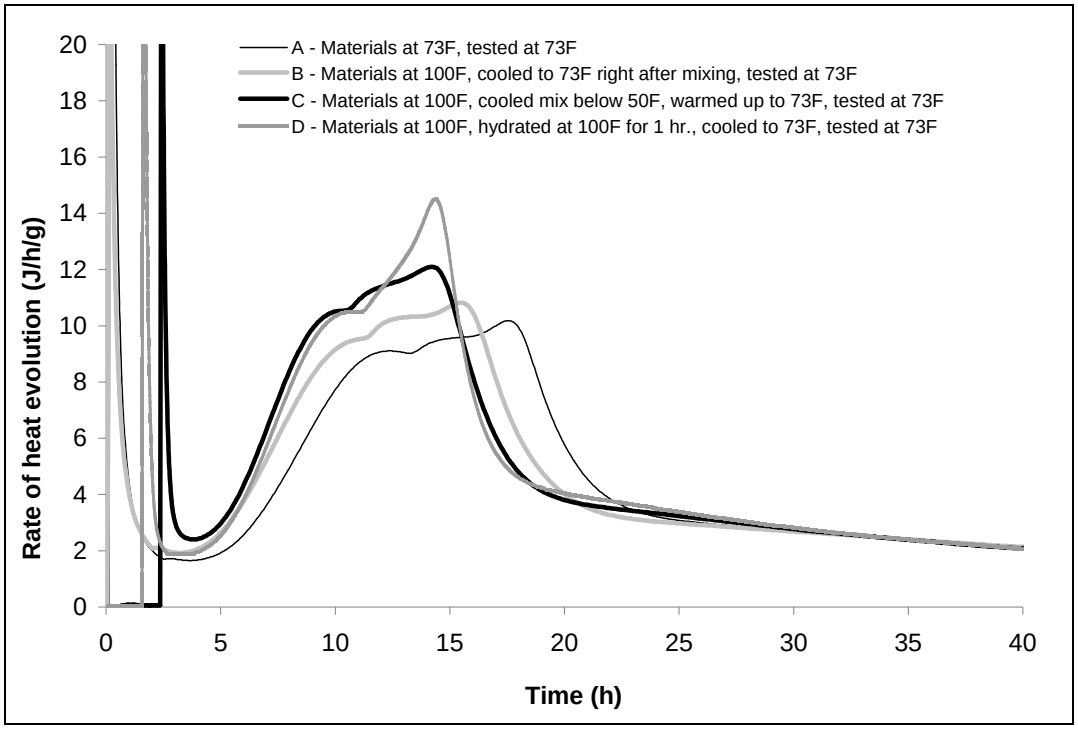


FIGURE D20 Rate of heat evolution curves for isothermal calorimetry Mixture 21 (C ash Parish + Naph)

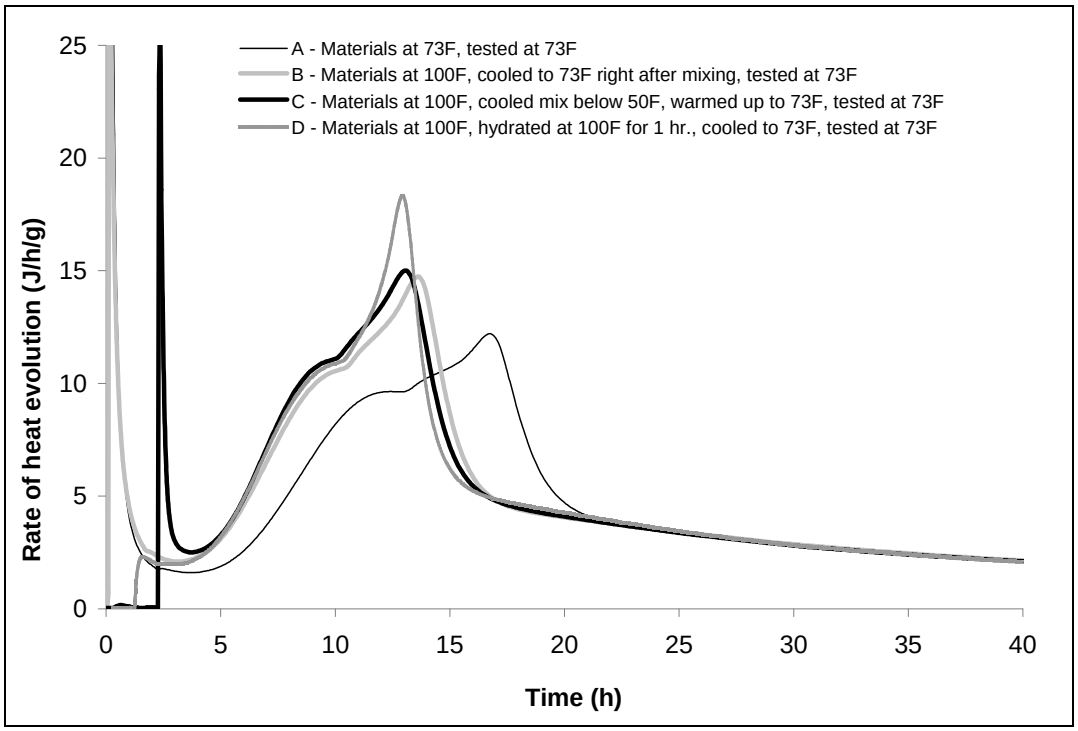


FIGURE D21 Rate of heat evolution curves for isothermal calorimetry Mixture 22 (C ash Parish + Poly)

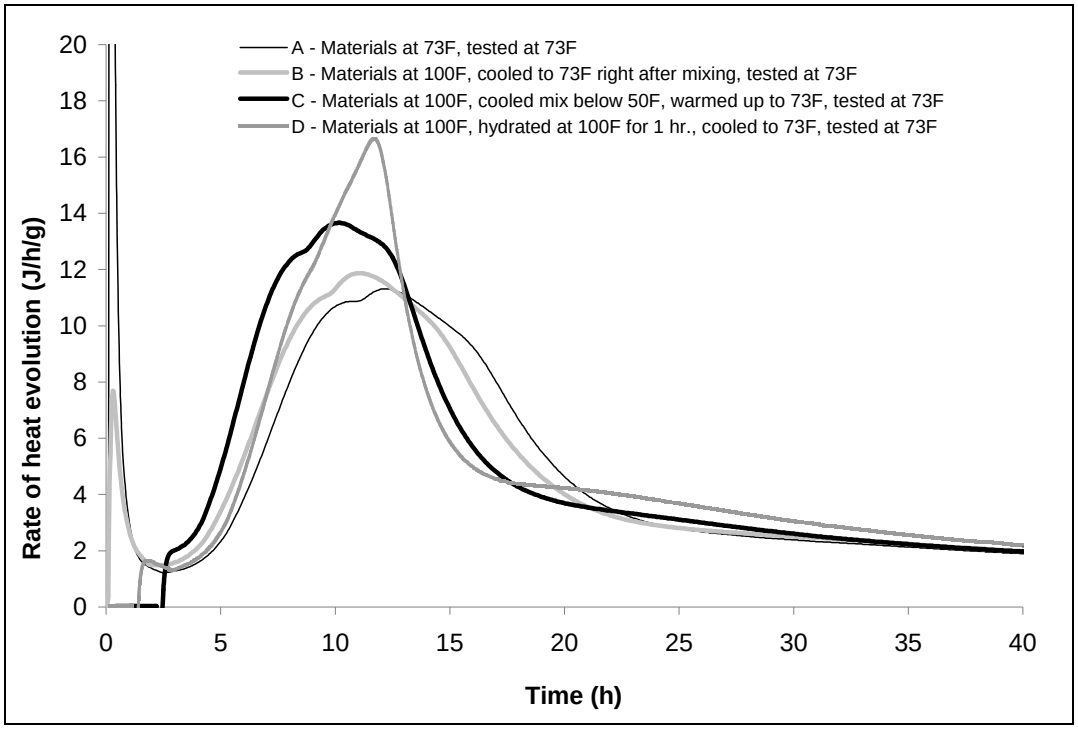


FIGURE D22 Rate of heat evolution curves for isothermal calorimetry Mixture 23 (F ash Big Brown + WR)

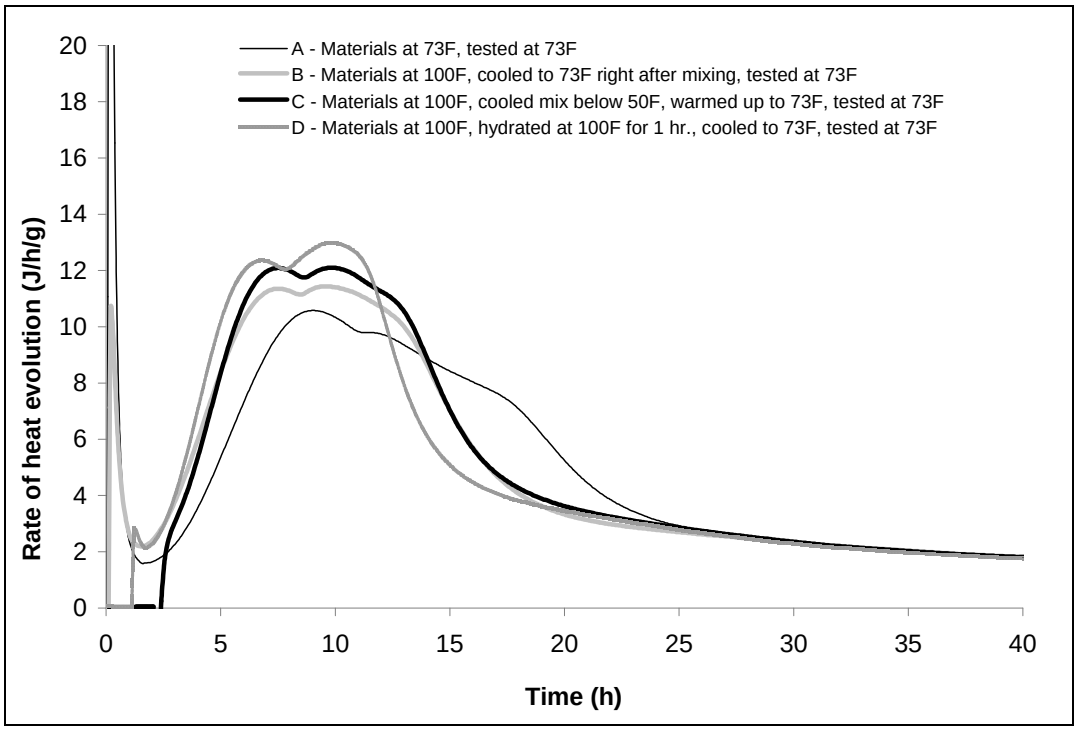


FIGURE D23 Rate of heat evolution curves for isothermal calorimetry Mixture 24 (F ash Big Brown + MRWR)

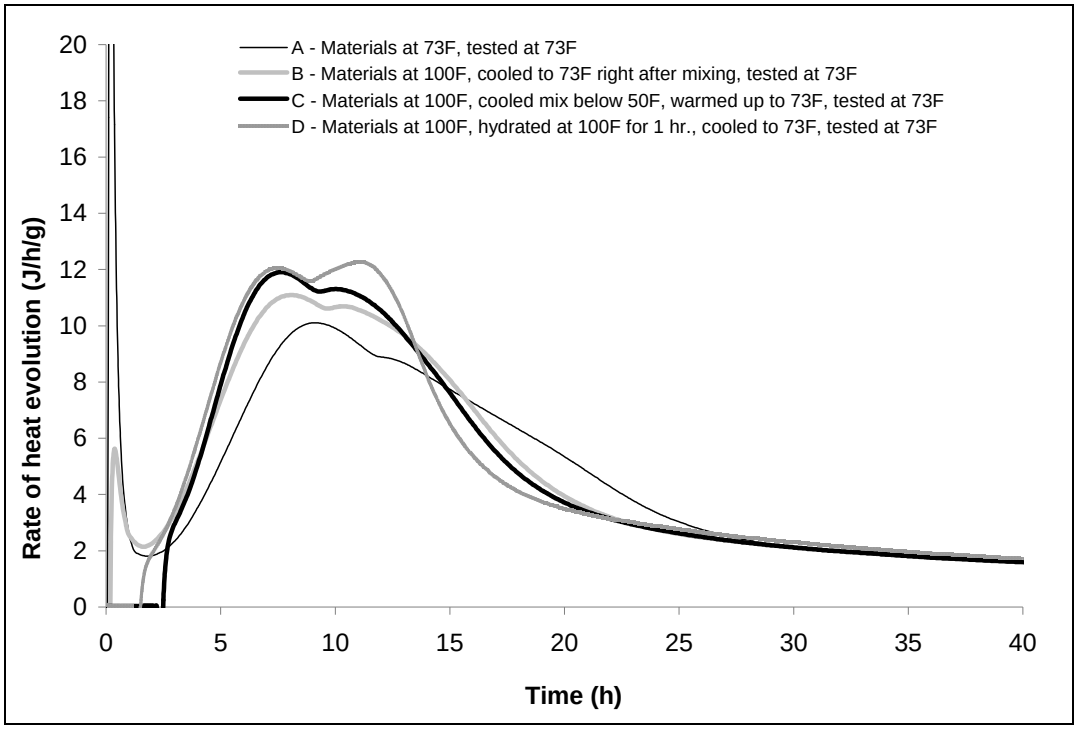


FIGURE D24 Rate of heat evolution curves for isothermal calorimetry Mixture 25 (F ash Big Brown + Naph)

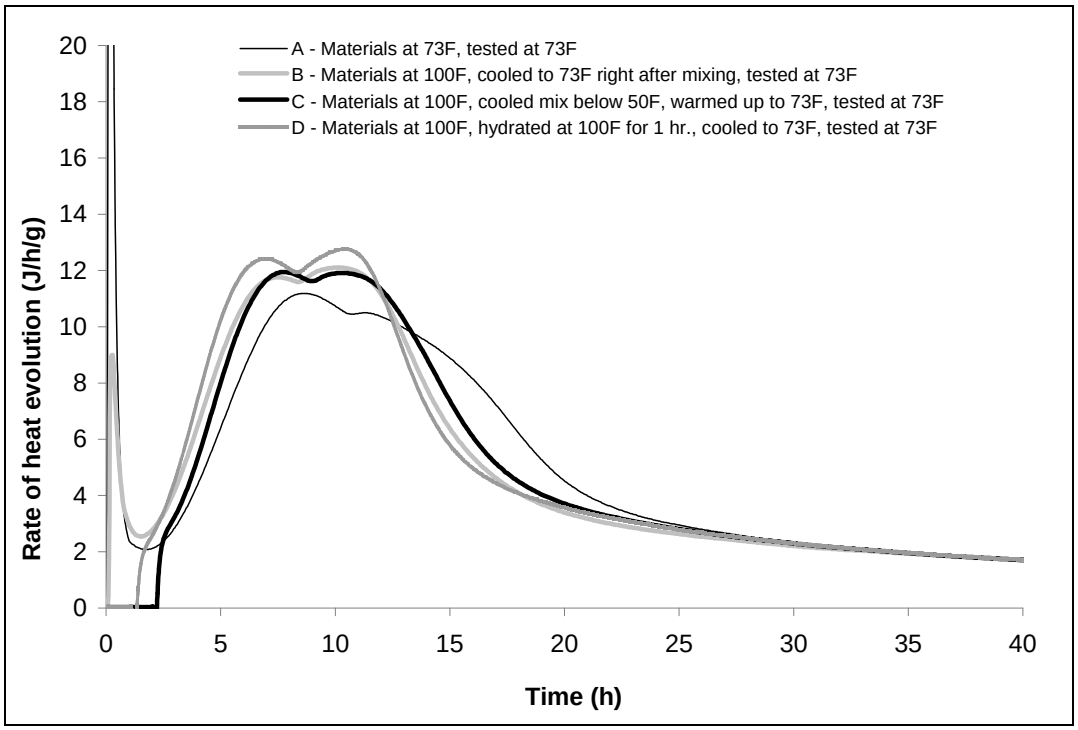


FIGURE D25 Rate of heat evolution curves for isothermal calorimetry Mixture 26 (F ash Big Brown + Poly)

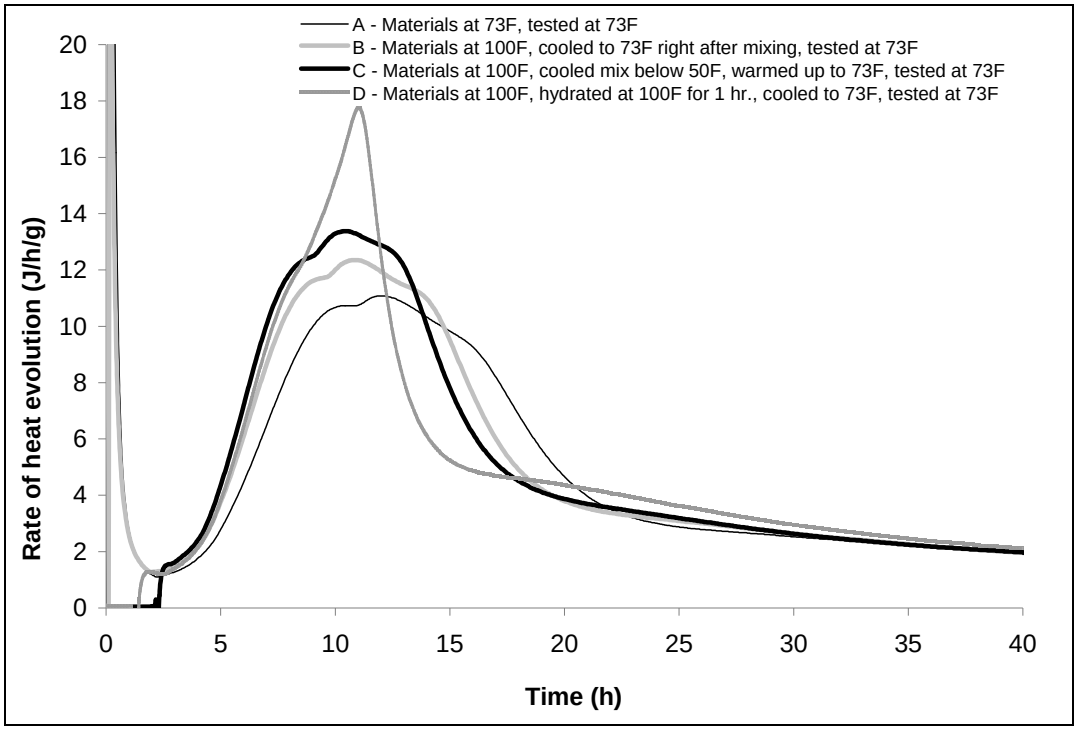


FIGURE D26 Rate of heat evolution curves for isothermal calorimetry Mixture 27 (F ash Martin Lake + WR)

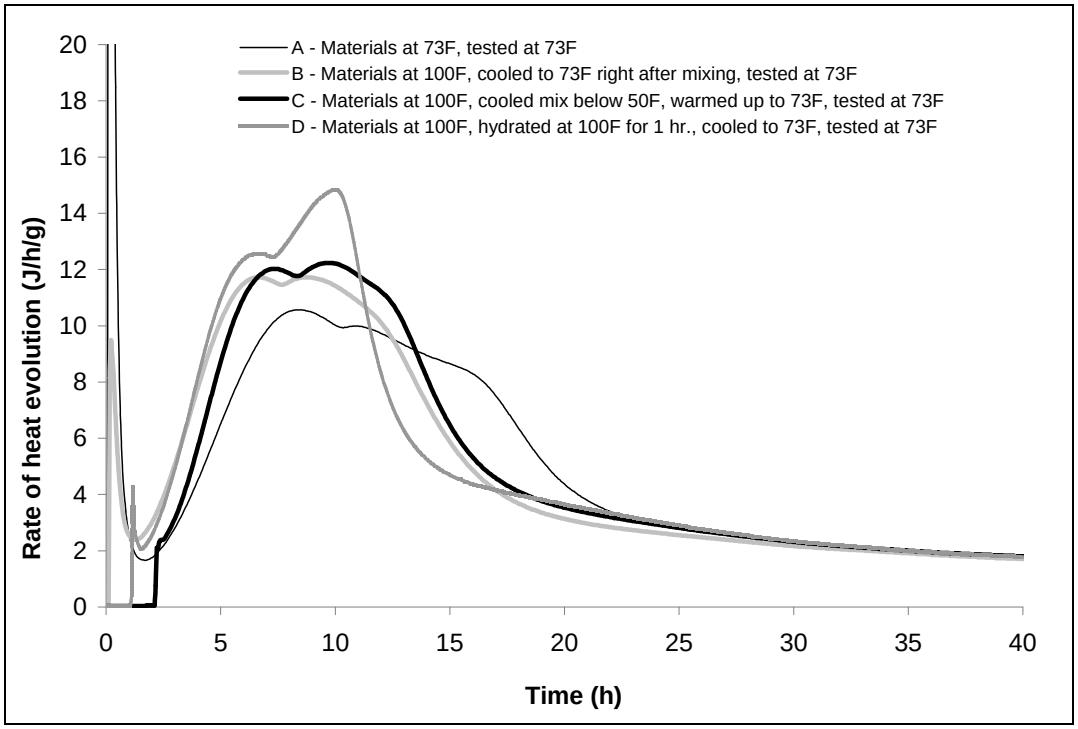


FIGURE D27 Rate of heat evolution curves for isothermal calorimetry Mixture 28 (F ash Martin Lake + MRWR)

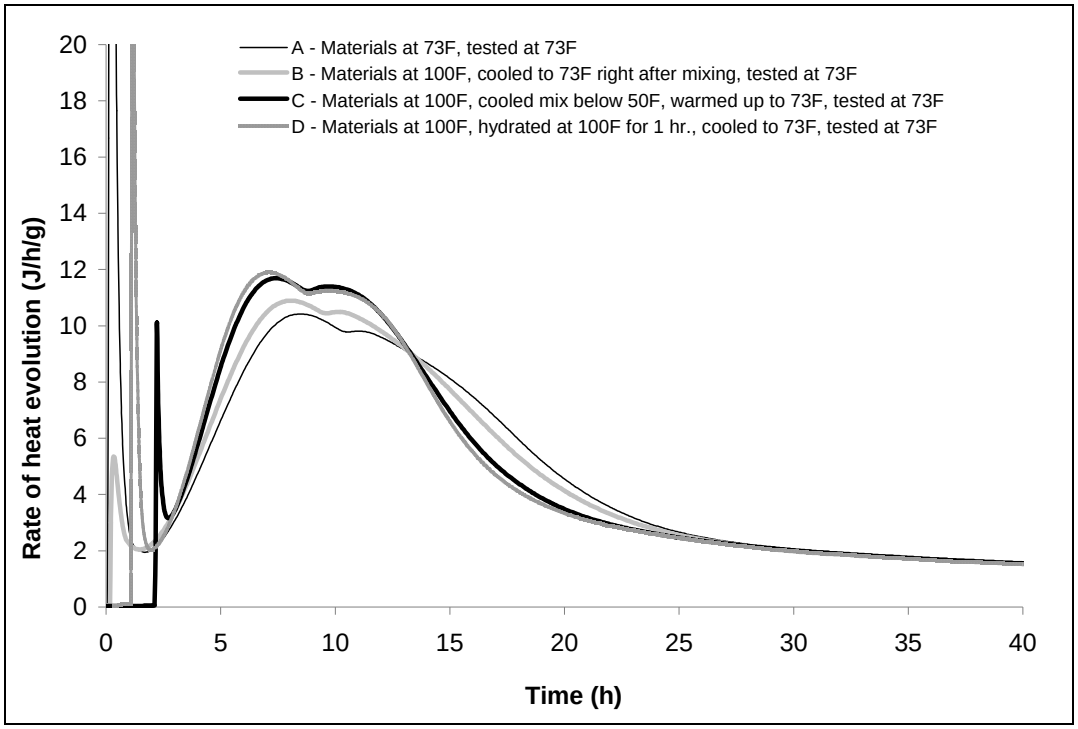


FIGURE D28 Rate of heat evolution curves for isothermal calorimetry Mixture 29 (F ash Martin Lake + Naph)

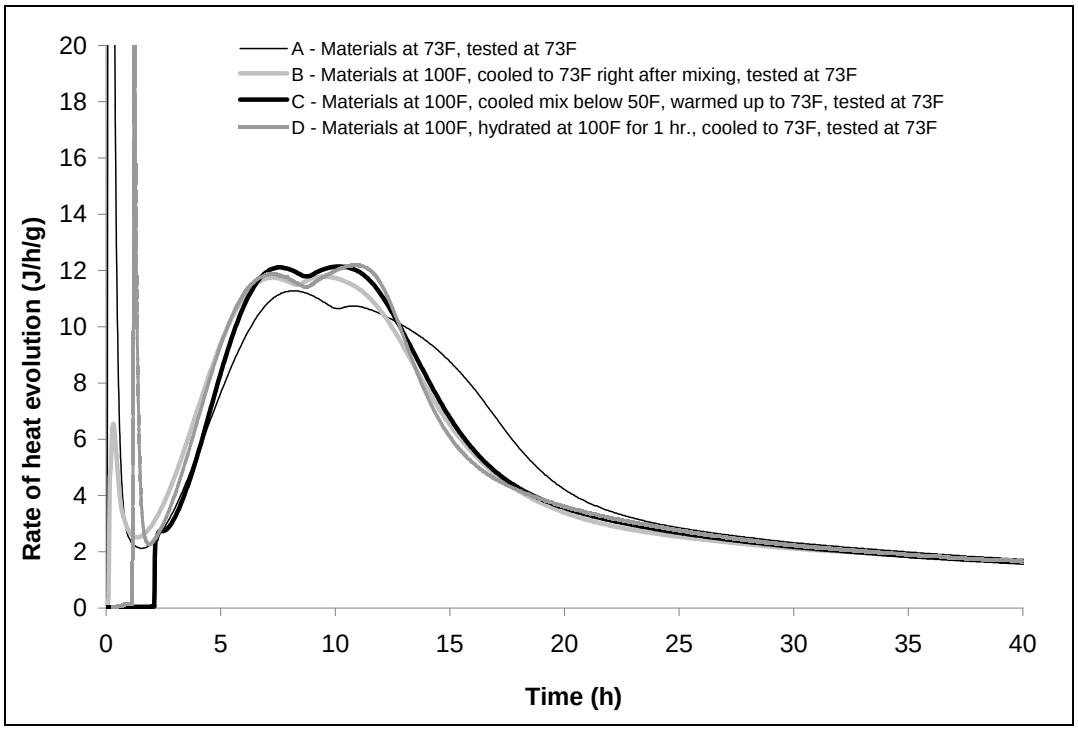


FIGURE D29 Rate of heat evolution curves for isothermal calorimetry Mixture 30 (F ash Martin Lake + Poly)

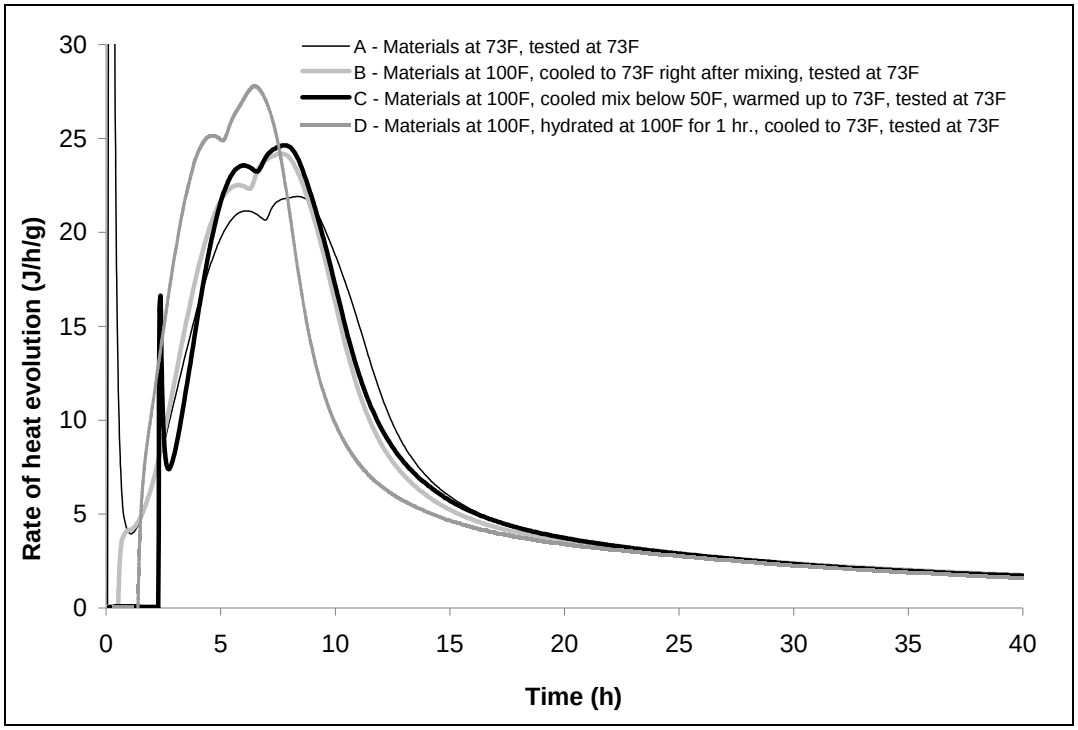


FIGURE D30 Rate of heat evolution curves for isothermal calorimetry Mixture 31 (Control III)

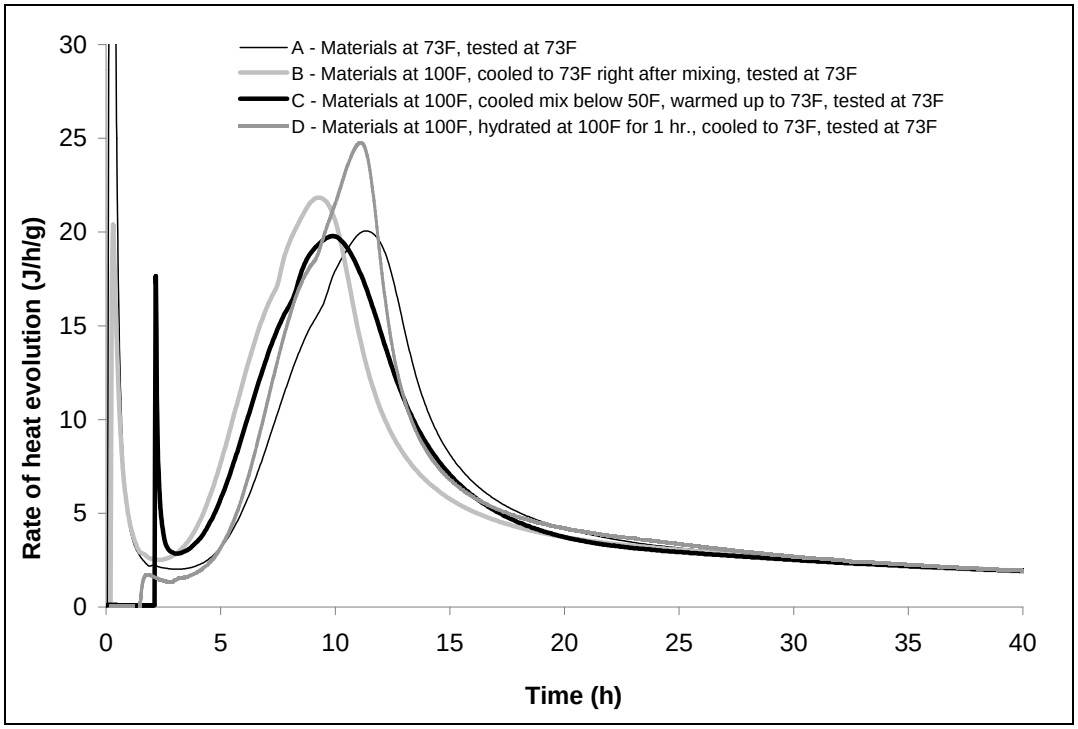


FIGURE D31 Rate of heat evolution curves for isothermal calorimetry Mixture 32 (F ash Big Brown + Naph + Retarder)

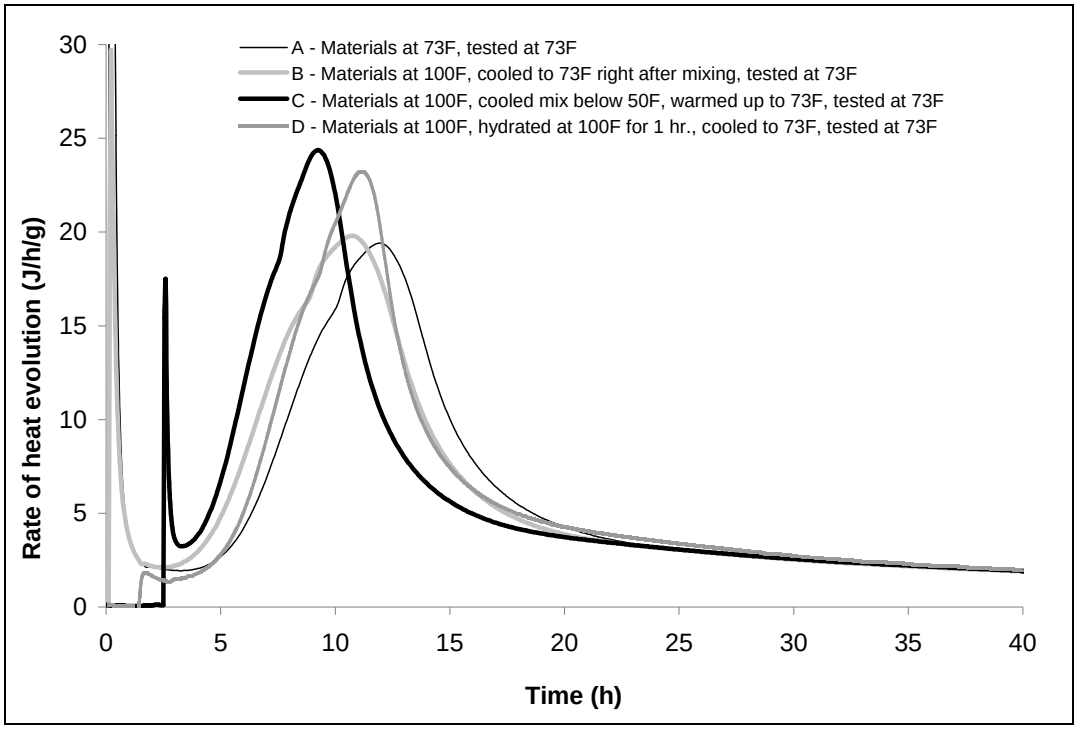


FIGURE D32 Rate of heat evolution curves for isothermal calorimetry Mixture 33 (F ash Big Brown + Poly + Retarder)

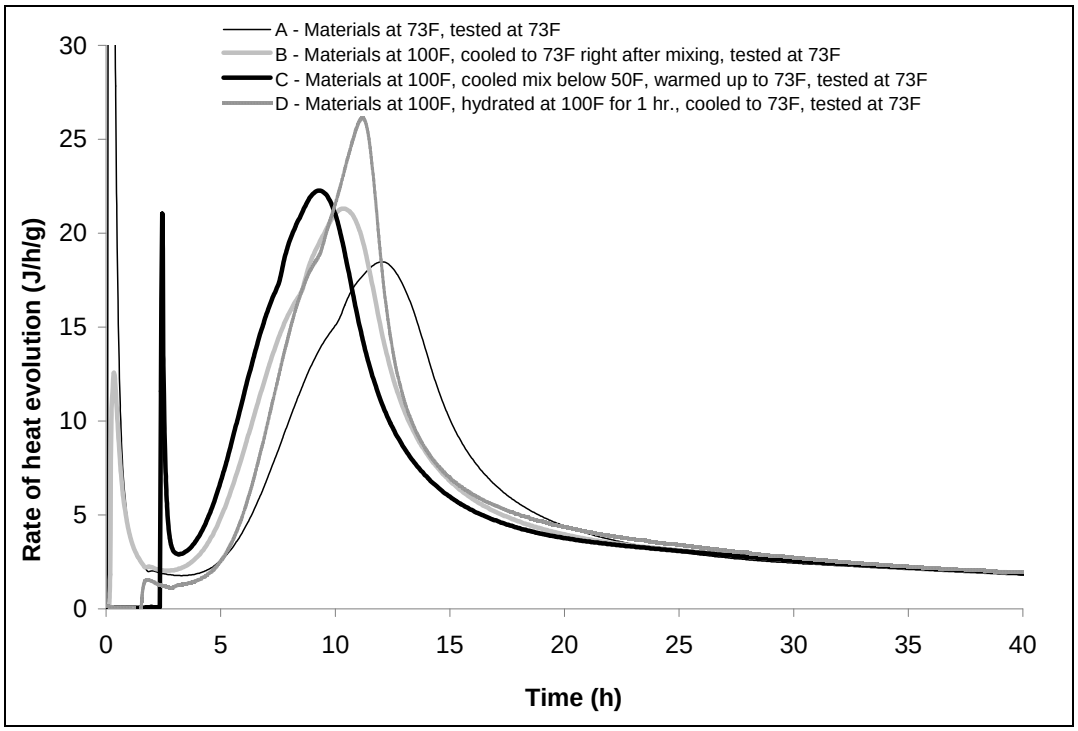


FIGURE D33 Rate of heat evolution curves for isothermal calorimetry Mixture 34 (F ash Martin Lake + Naph + Retarder)

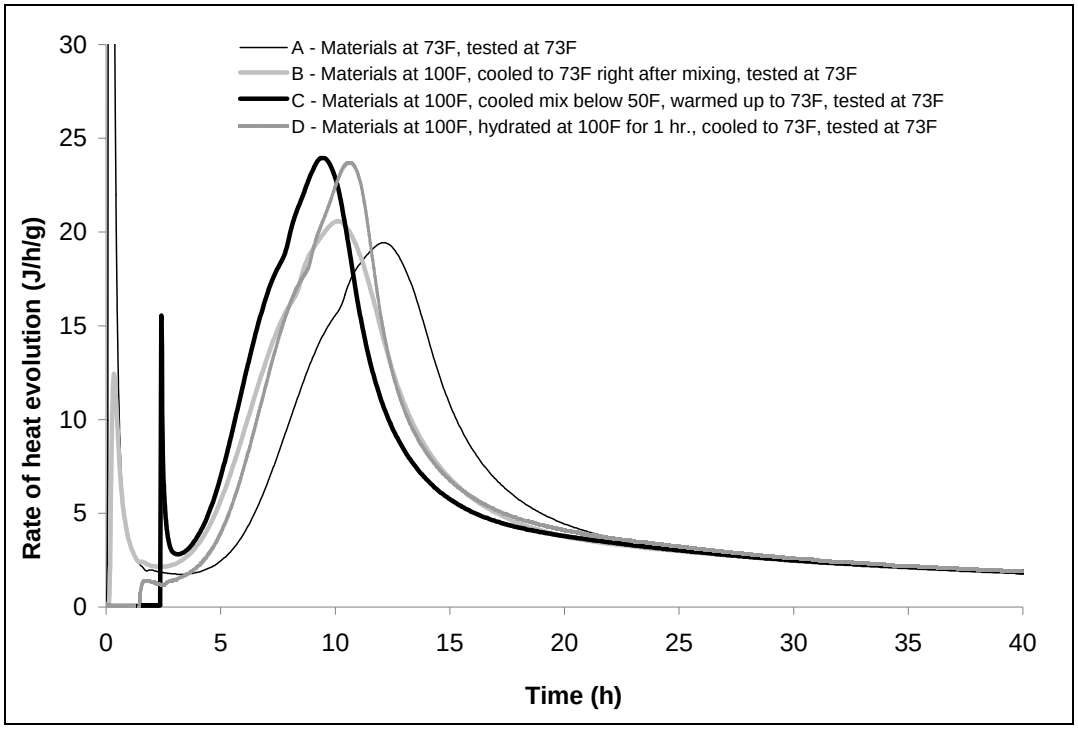


FIGURE D34 Rate of heat evolution curves for isothermal calorimetry Mixture 35 (F ash Martin Lake + Poly + Retarder)

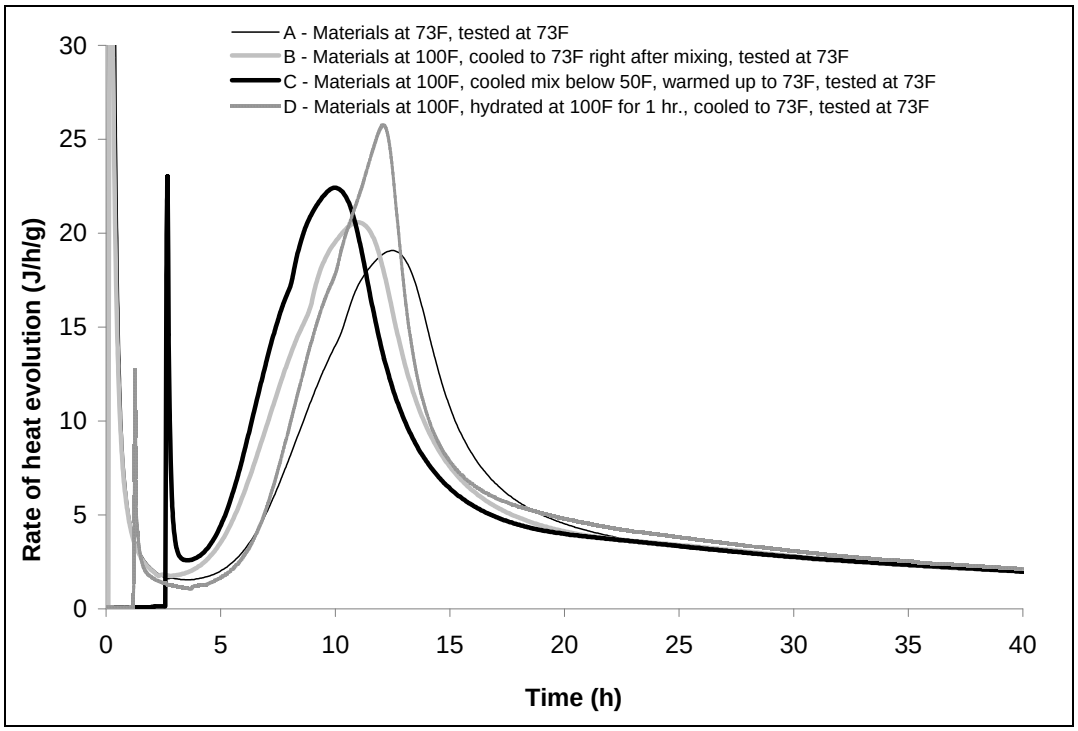


FIGURE D35 Rate of heat evolution curves for isothermal calorimetry Mixture 36 (F ash Big Brown + Naph + MRWR + Retarder)

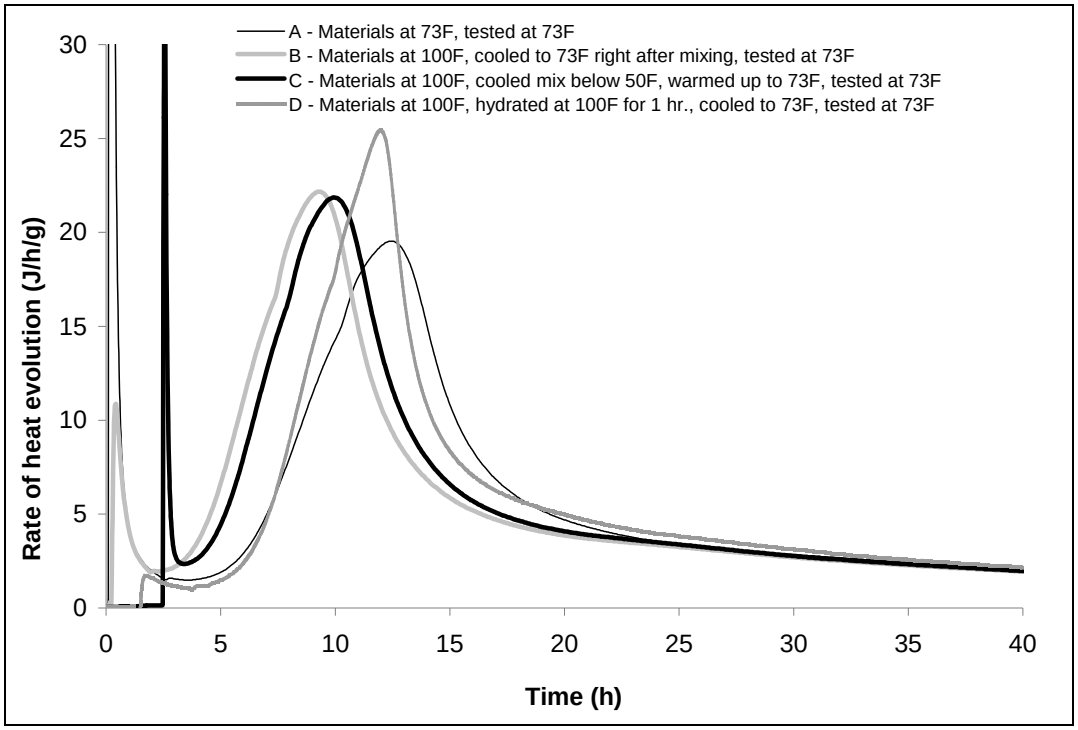


FIGURE D36 Rate of heat evolution curves for isothermal calorimetry Mixture 37 (F ash Martin Lake + Naph + MRWR + Retarder)

APPENDIX E: X-ray Diffraction (XRD)

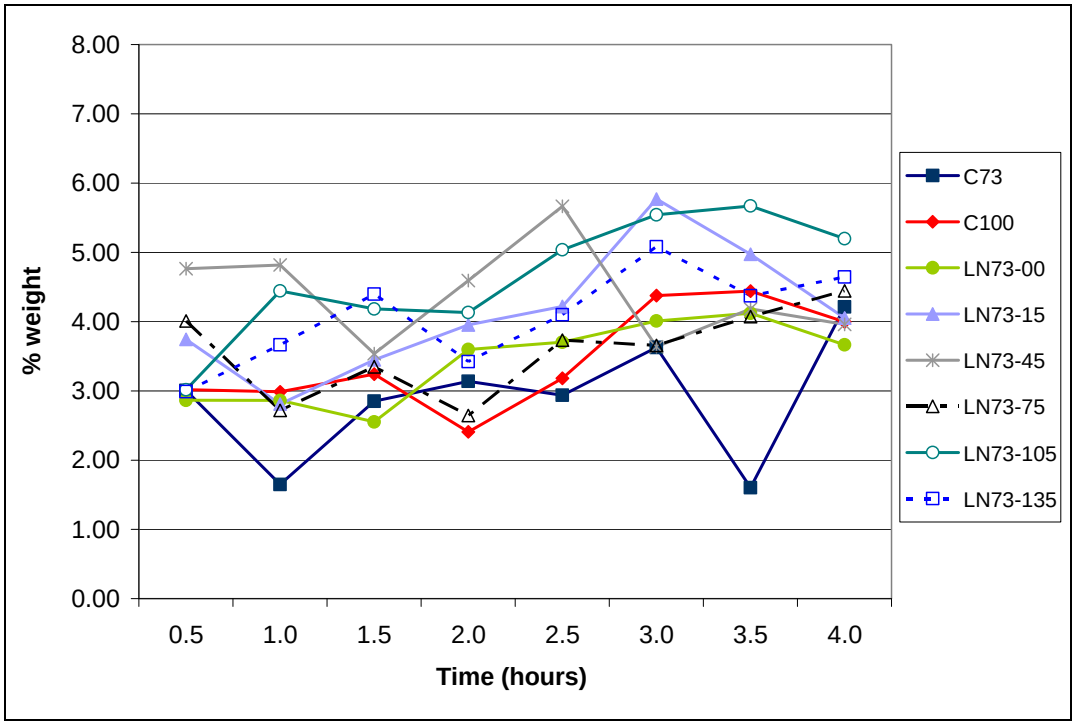


FIGURE E1 Ettringite analysis by x-ray diffraction of cement paste mixtures cooled to 73°F with LN at varying times

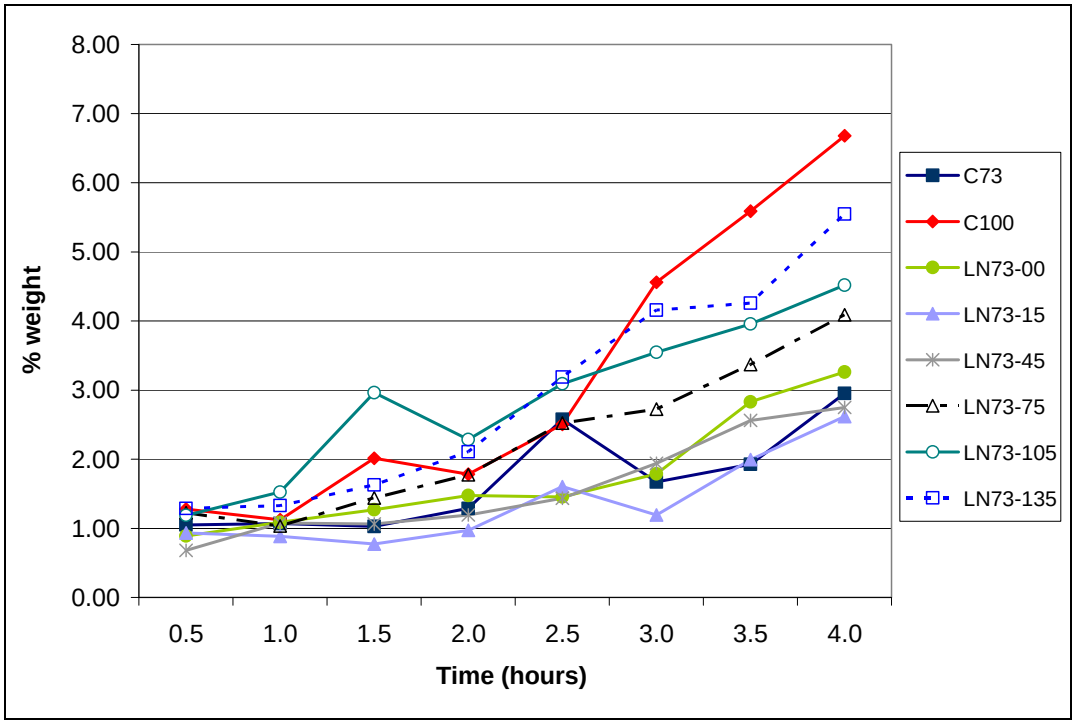


FIGURE E2 Calcium hydroxide analysis by x-ray diffraction of cement paste mixtures cooled to 73°F with LN at varying times

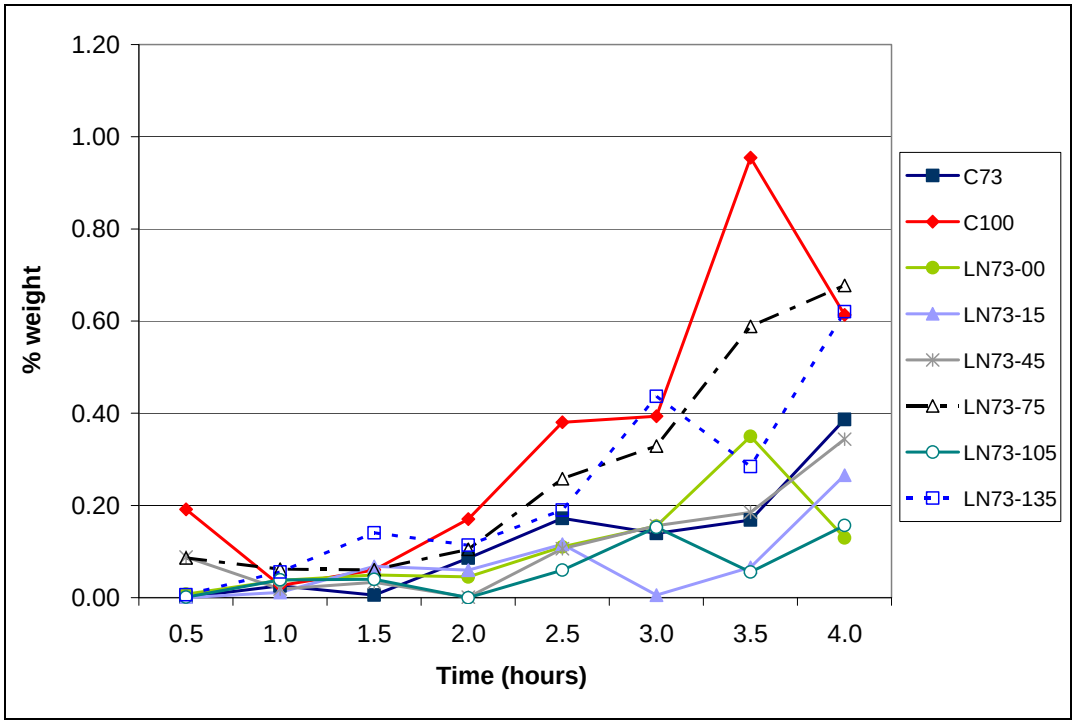


FIGURE E3 Monosulfoaluminate analysis by x-ray diffraction of cement paste mixtures cooled to 73°F with LN at varying times

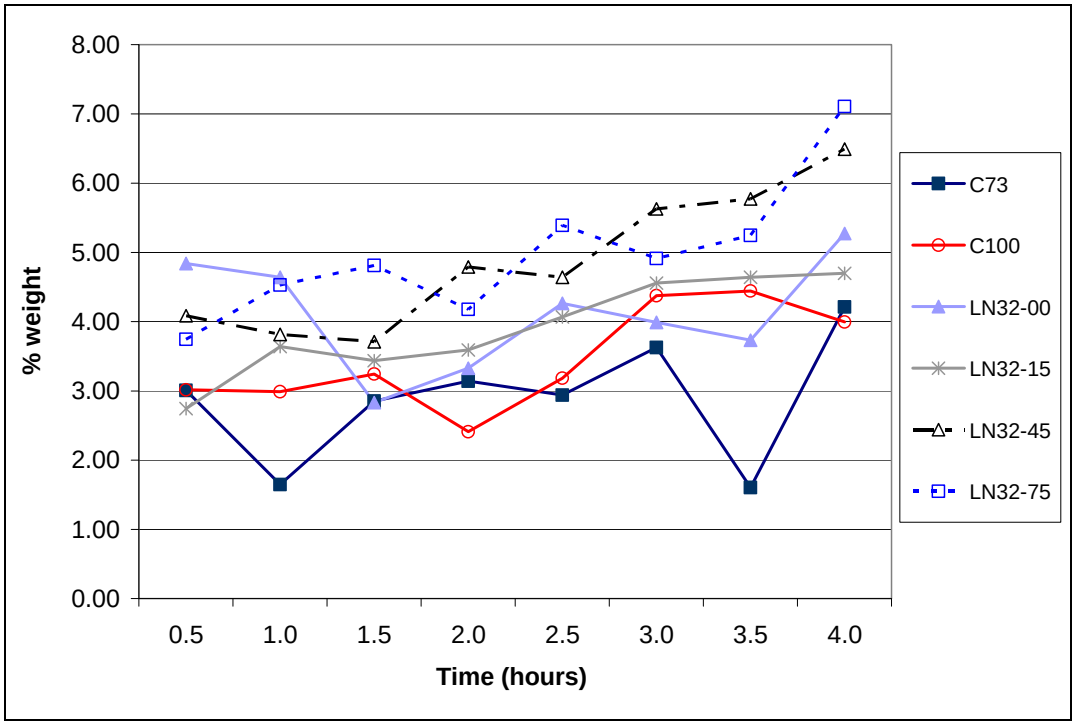


FIGURE E4 Ettringite analysis by x-ray diffraction of cement paste mixtures cooled to 32°F with LN at varying times

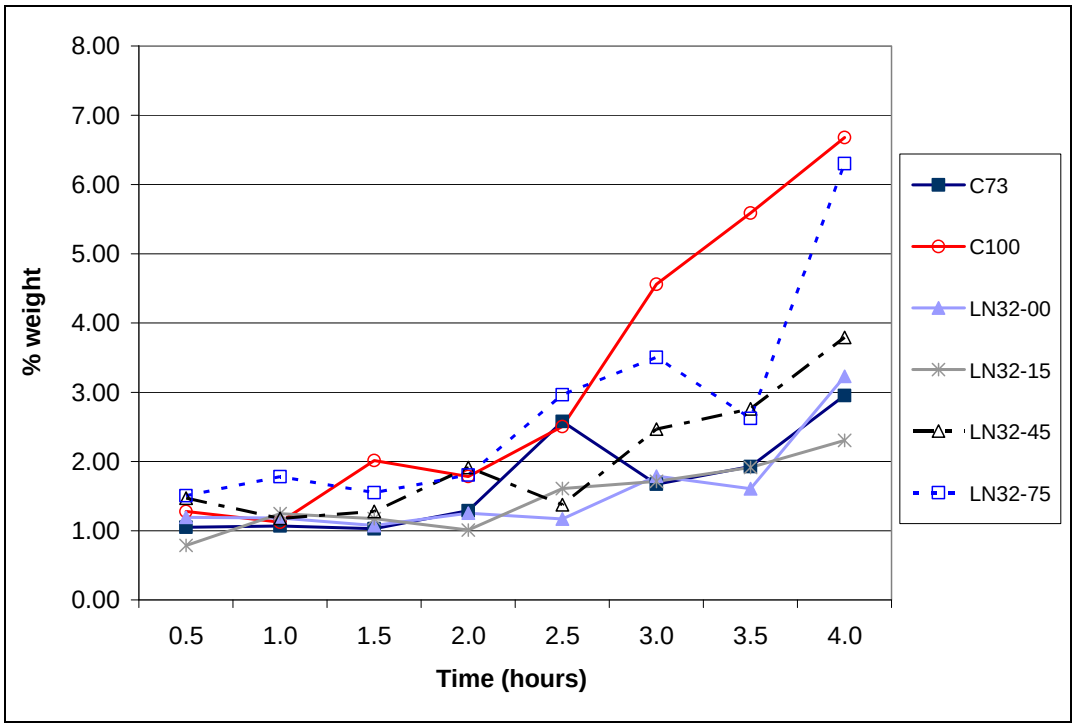


FIGURE E5 Calcium hydroxide analysis by x-ray diffraction of cement paste mixtures cooled to 32°F with LN at varying times

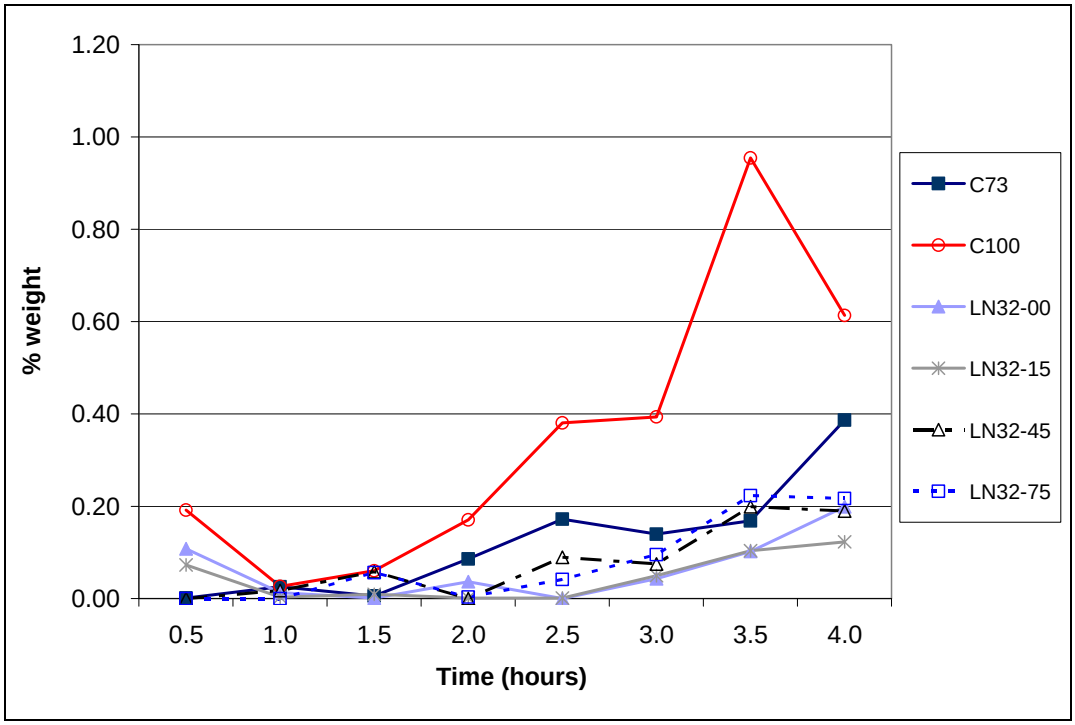


FIGURE E6 Monosulfoaluminate analysis by x-ray diffraction of cement paste mixtures cooled to 32°F with LN at varying times

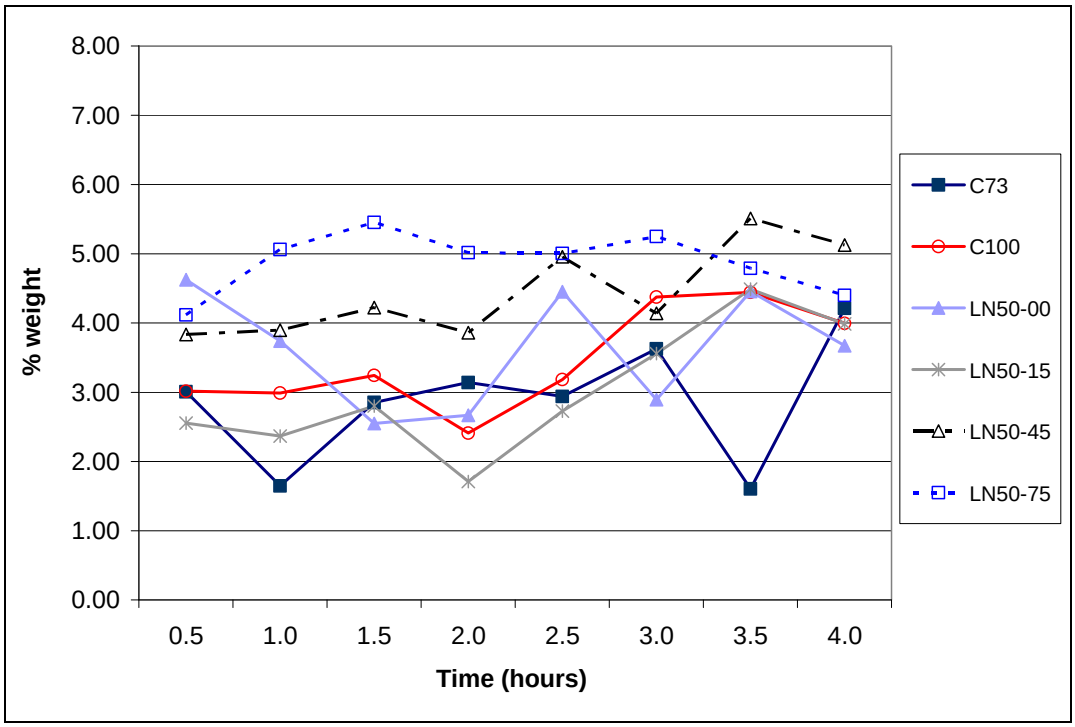


FIGURE E7 Ettringite analysis by x-ray diffraction of cement paste mixtures cooled to 50°F with LN at varying times

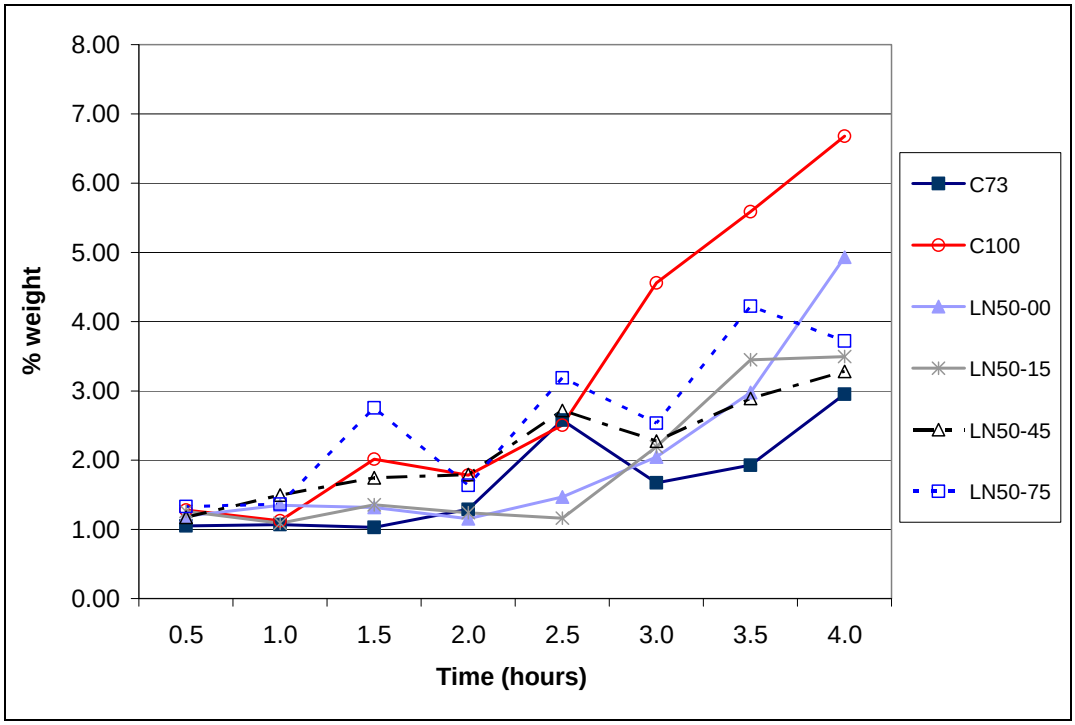


FIGURE E8 Calcium hydroxide analysis by x-ray diffraction of cement paste mixtures cooled to 50°F with LN at varying times

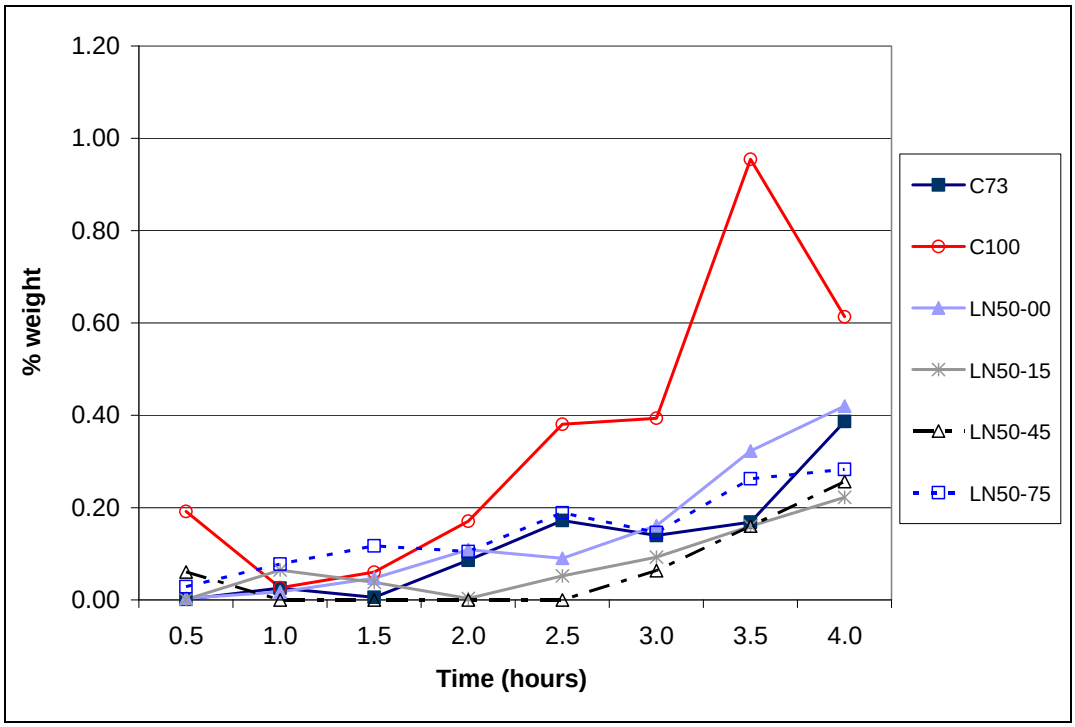


FIGURE E9 Monosulfoaluminate analysis by x-ray diffraction of cement paste mixtures cooled to 50°F with LN at varying times

APPENDIX F: Inductively Coupled Plasma (ICP)

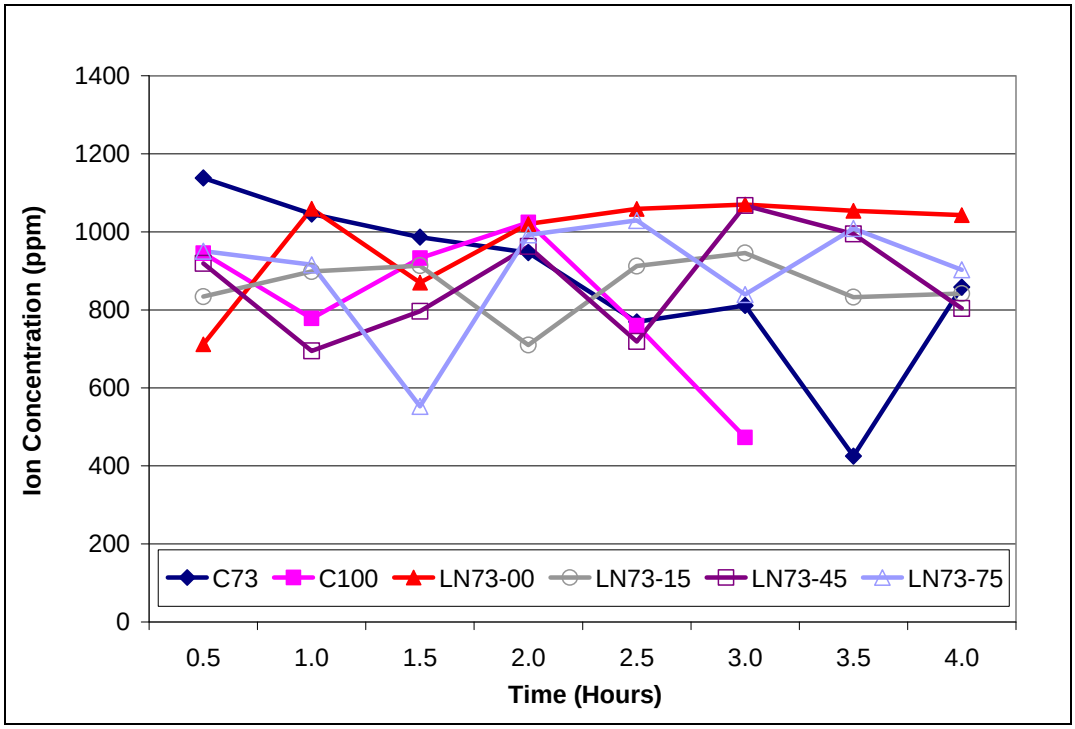


FIGURE F1 Calcium (Ca) concentrations for LN cement paste mixtures

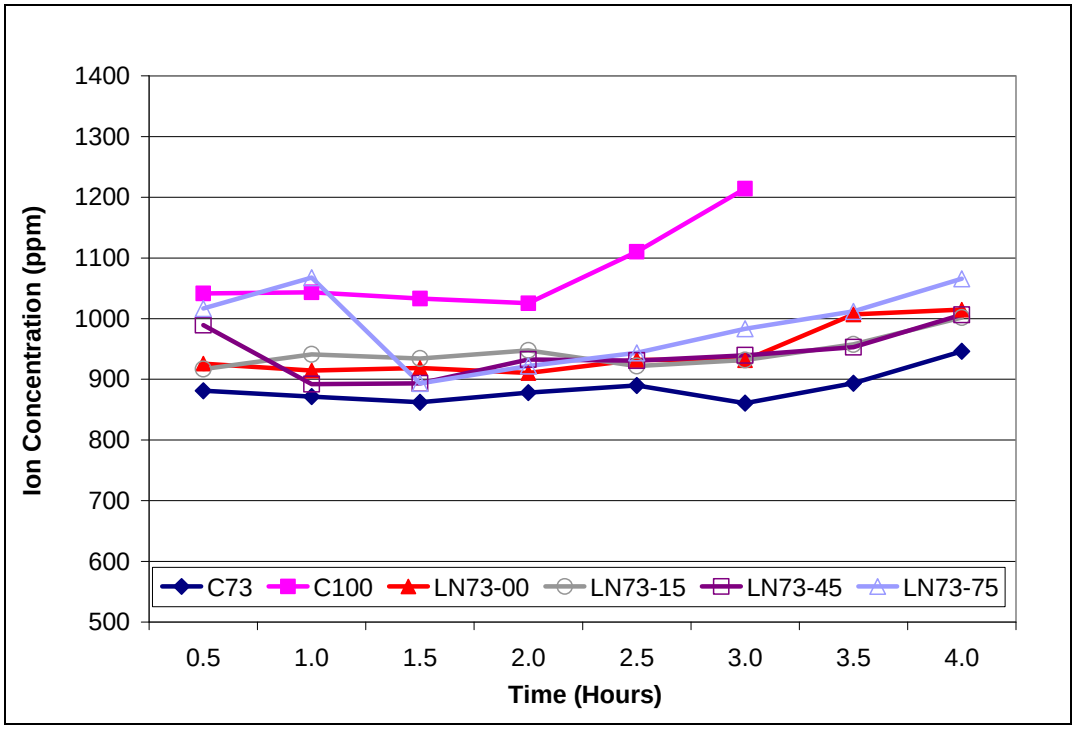


FIGURE F2 Sulfur (S) concentrations for LN cement paste mixtures

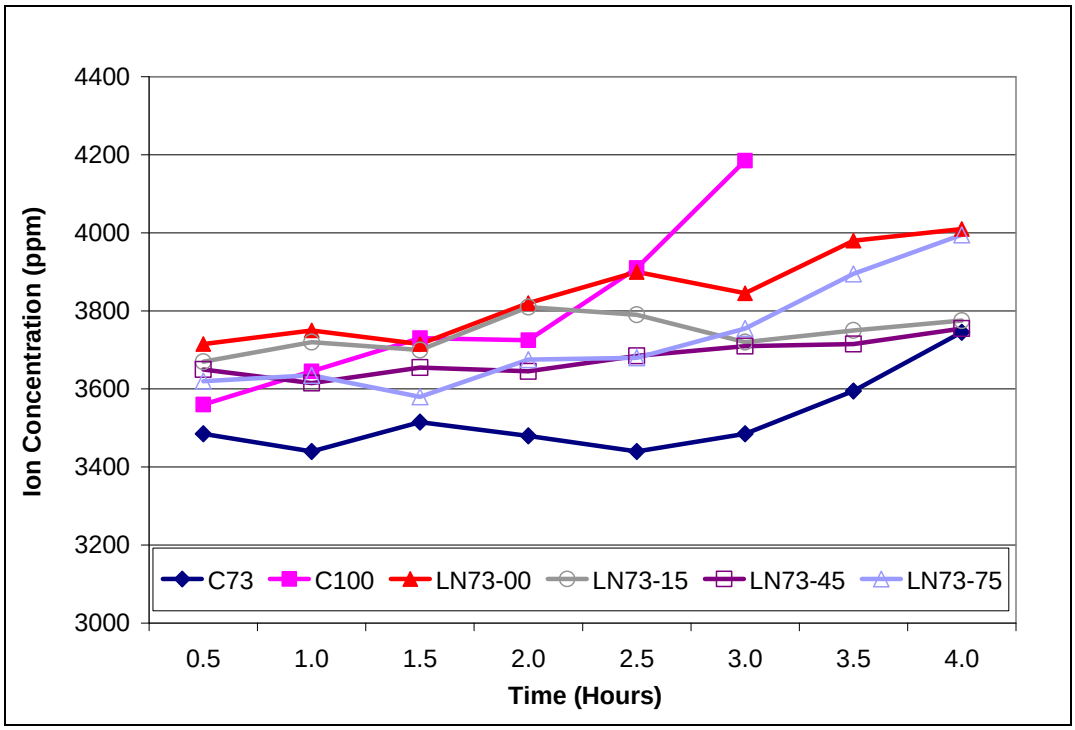


FIGURE F3 Potassium (K) concentrations for LN cement paste mixtures

APPENDIX G: Environmental Scanning Electron Microscopy (ESEM)

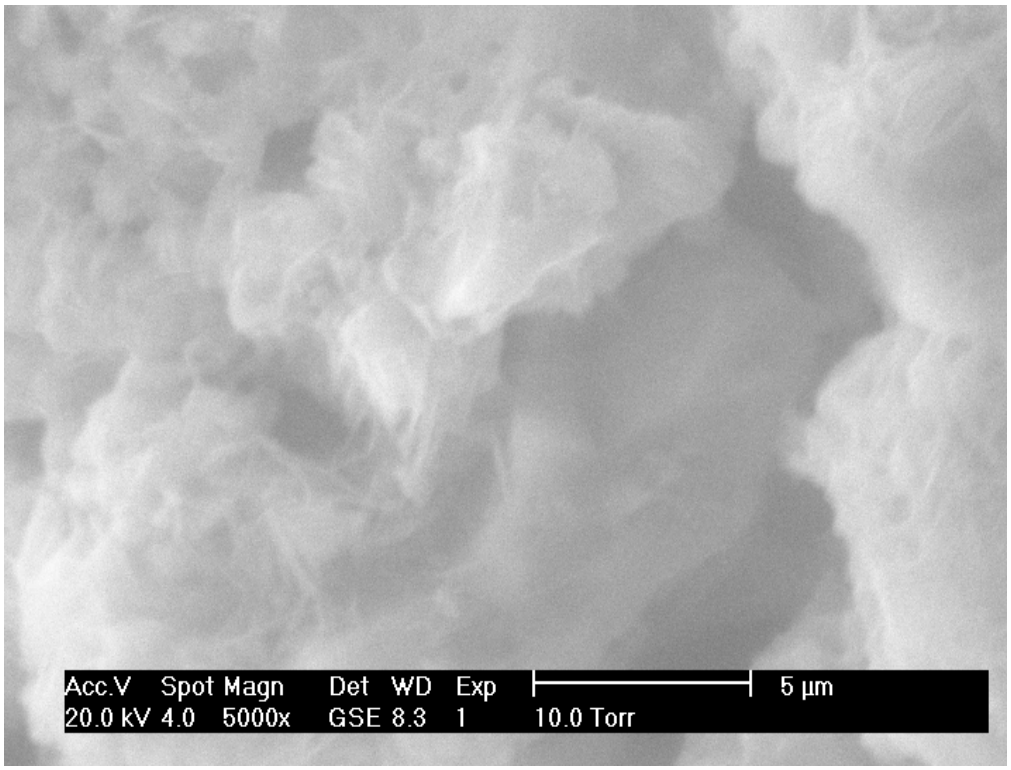


FIGURE G1 ESEM image of cement paste after 1 hour of hydration (C73)

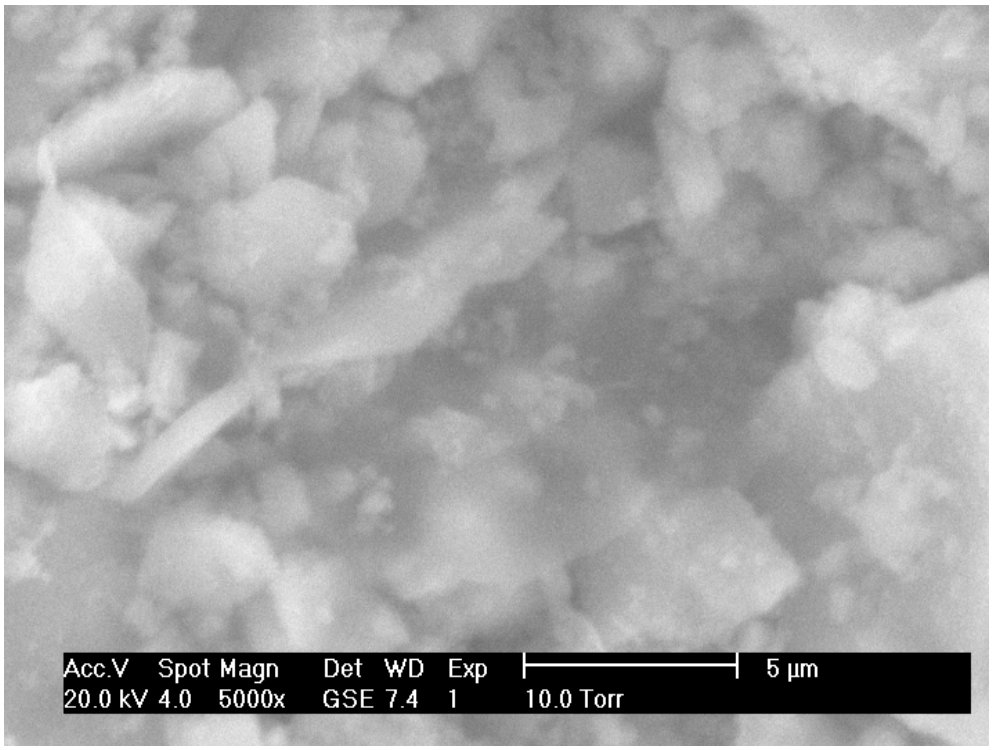


FIGURE G2 ESEM image of cement paste after 3 hours of hydration (C73)

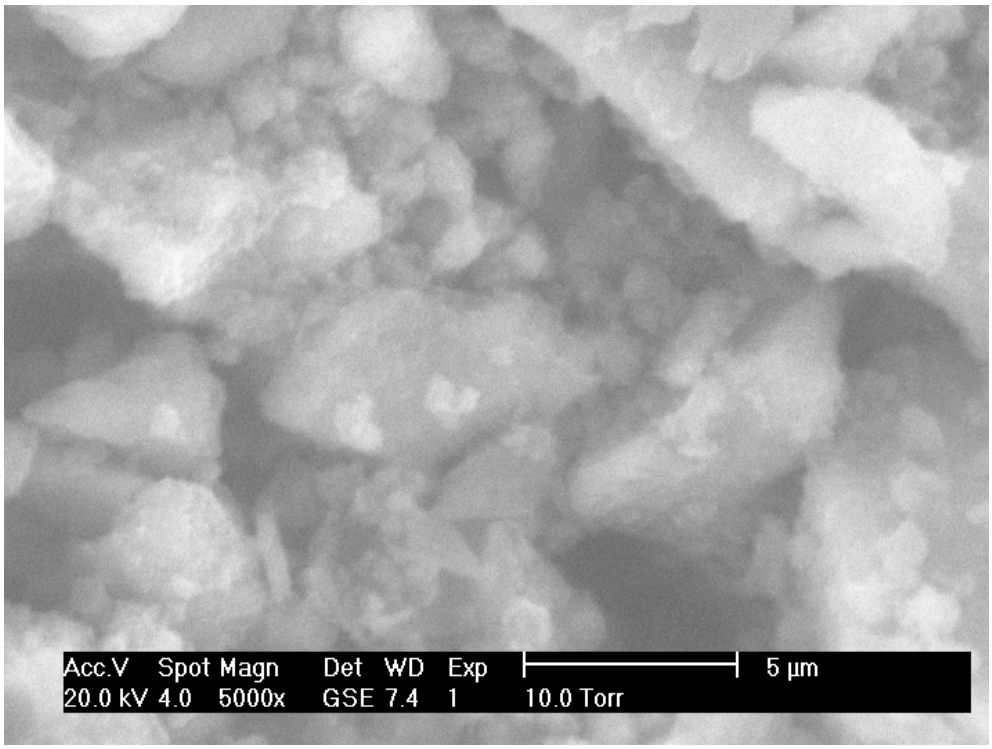


FIGURE G3 ESEM image of cement paste after 4 hours of hydration (C73)

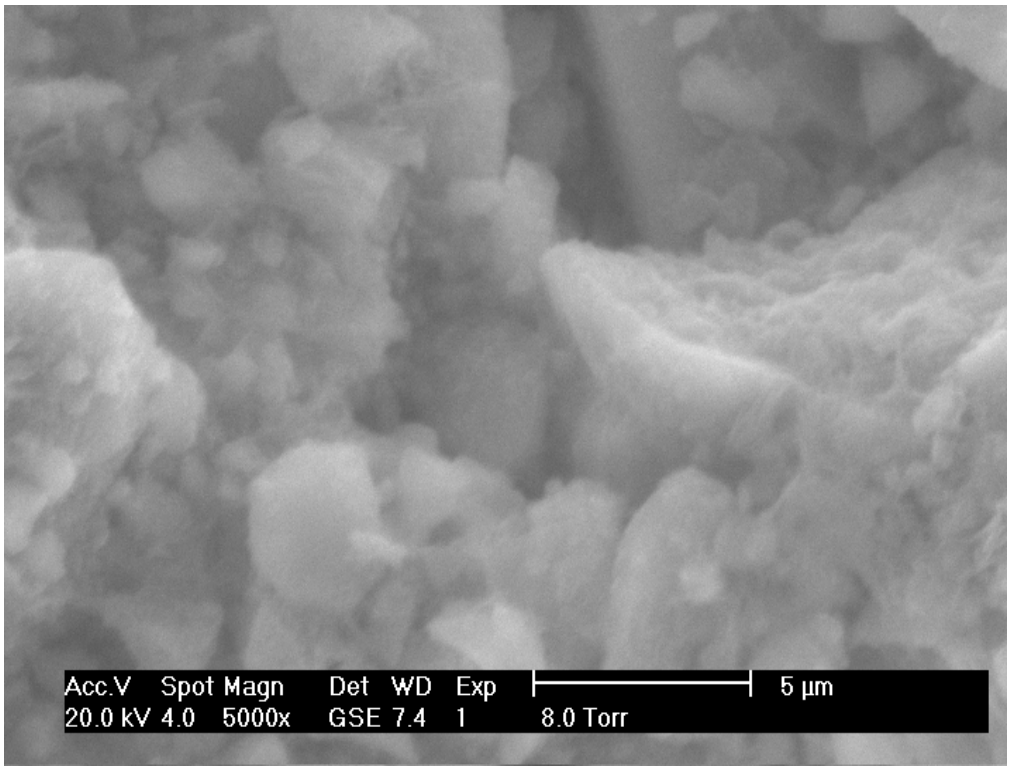


FIGURE G4 ESEM image of cement paste after 1 hour of hydration (LN73-00)

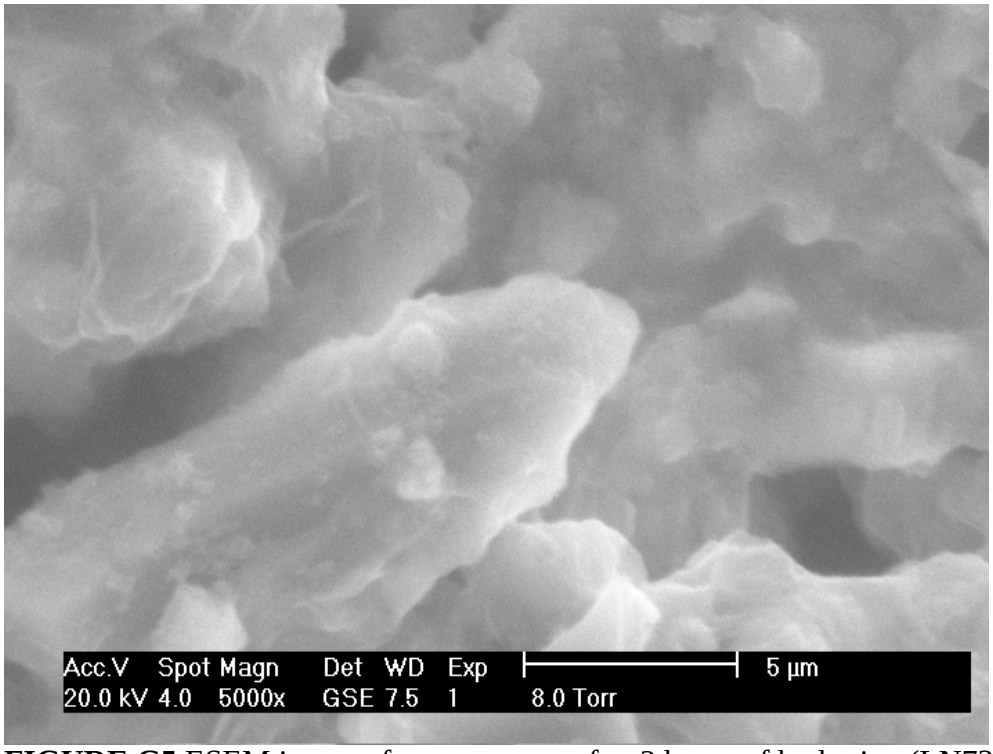


FIGURE G5 ESEM image of cement paste after 2 hours of hydration (LN73-00)

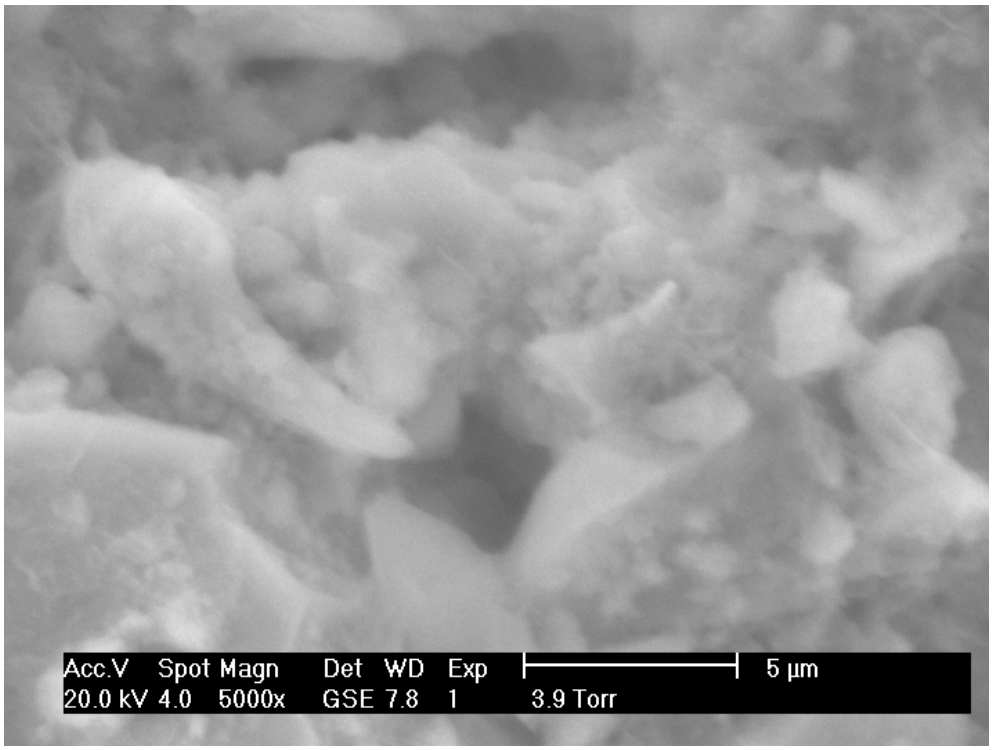


FIGURE G6 ESEM image of cement paste after 3 hours of hydration (LN73-00)

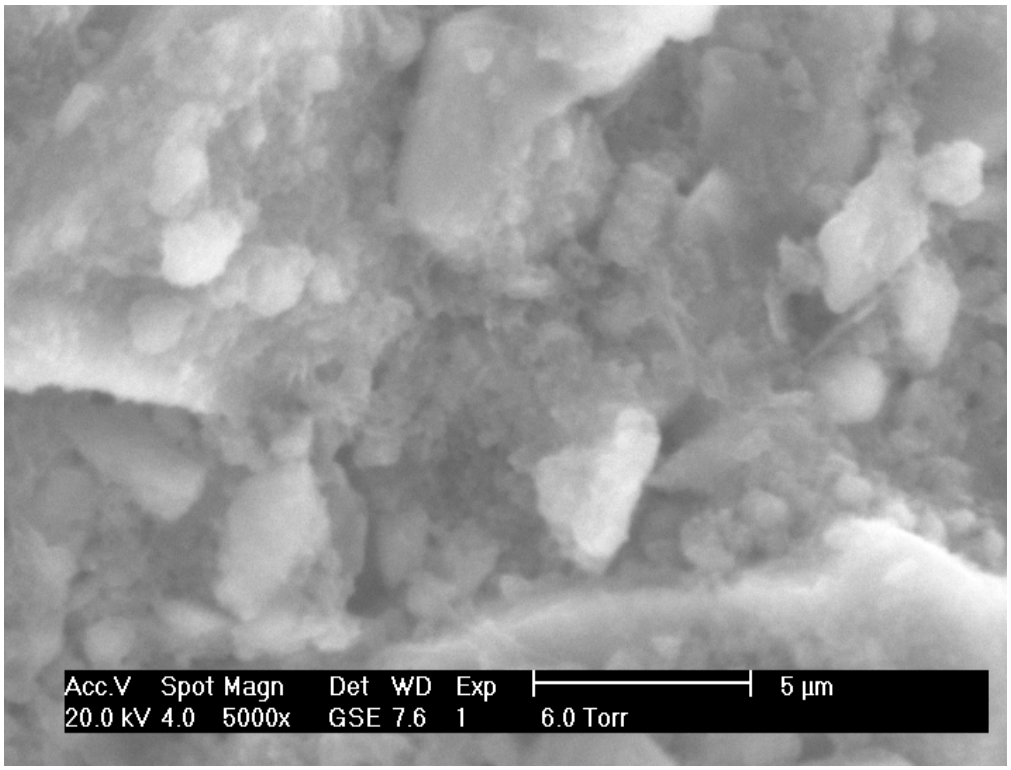


FIGURE G7 ESEM image of cement paste after 4 hours of hydration (LN73-00)

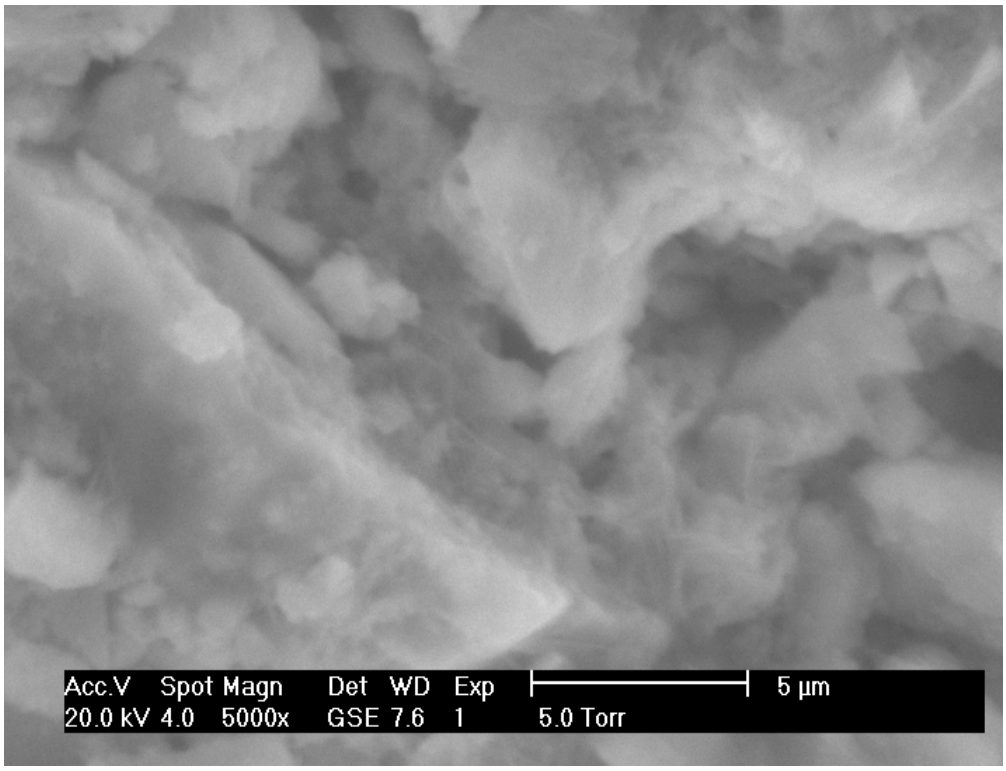


FIGURE G8 ESEM image of cement paste after 1 hour of hydration (LN50-00)

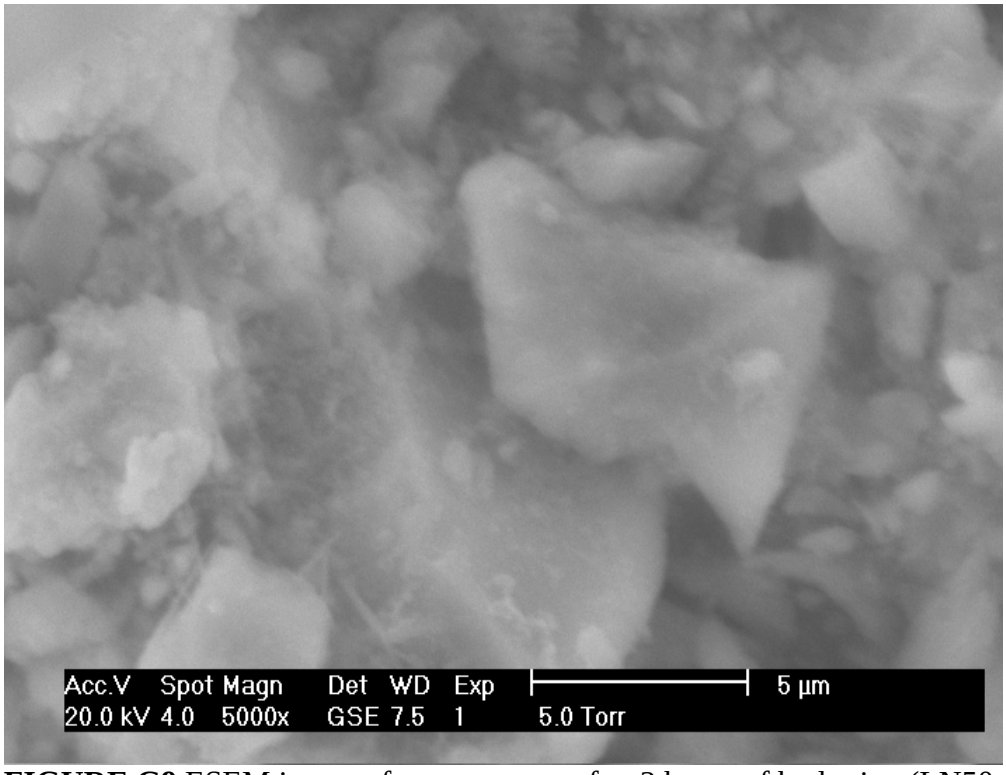


FIGURE G9 ESEM image of cement paste after 2 hours of hydration (LN50-00)

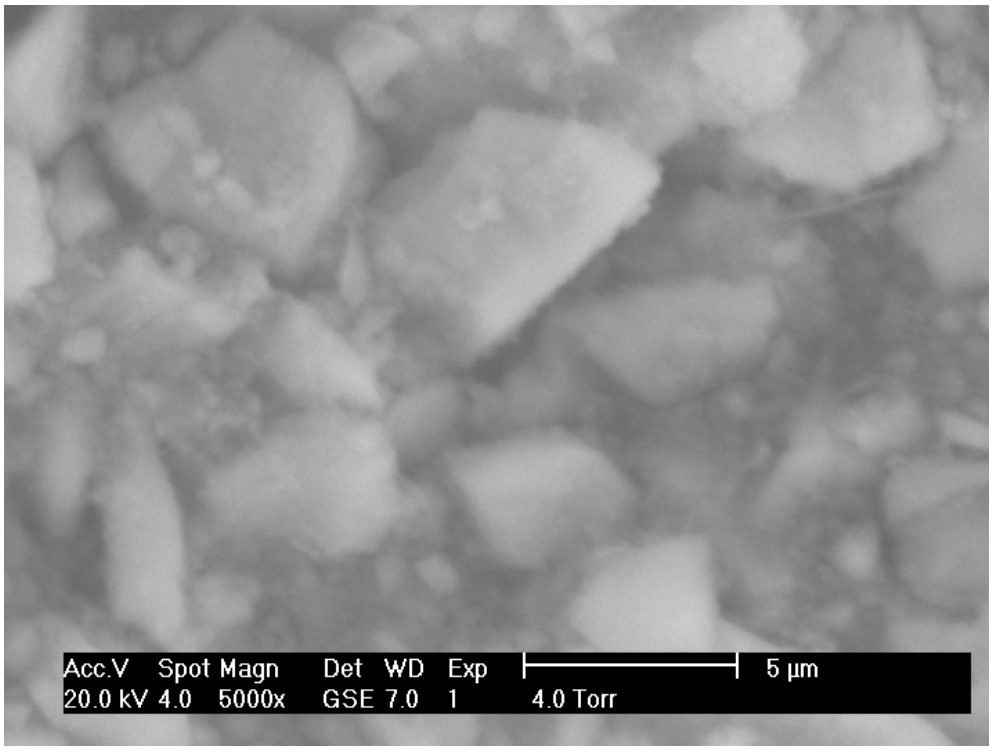


FIGURE G10 ESEM image of cement paste after 3 hours of hydration (LN50-00)

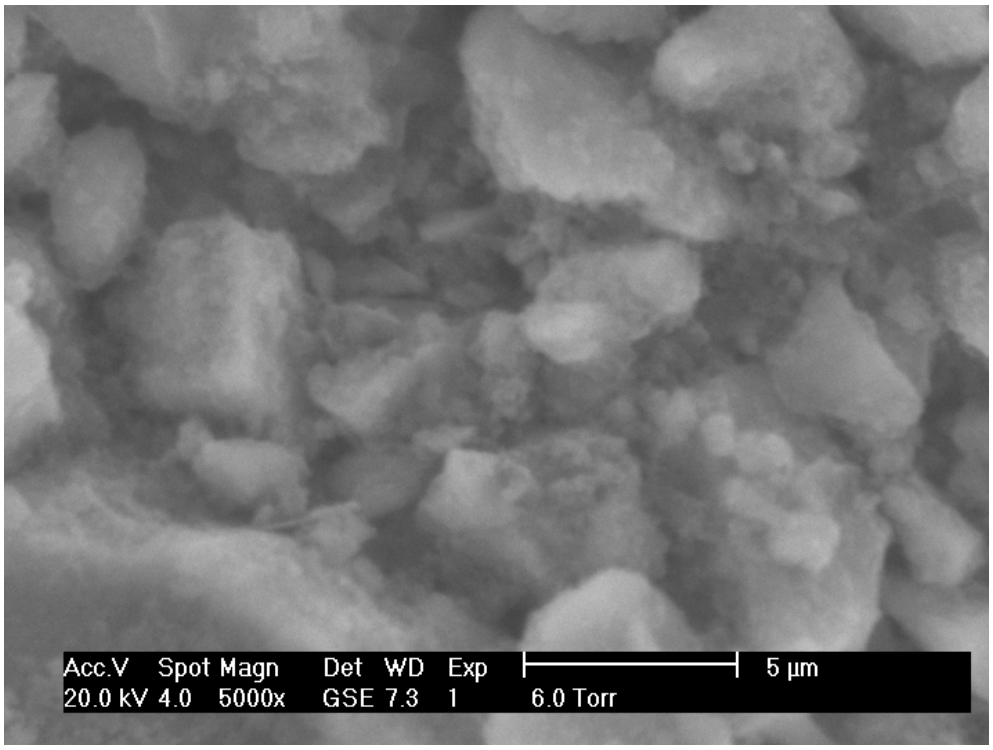


FIGURE G11 ESEM image of cement paste after 4 hours of hydration (LN50-00)

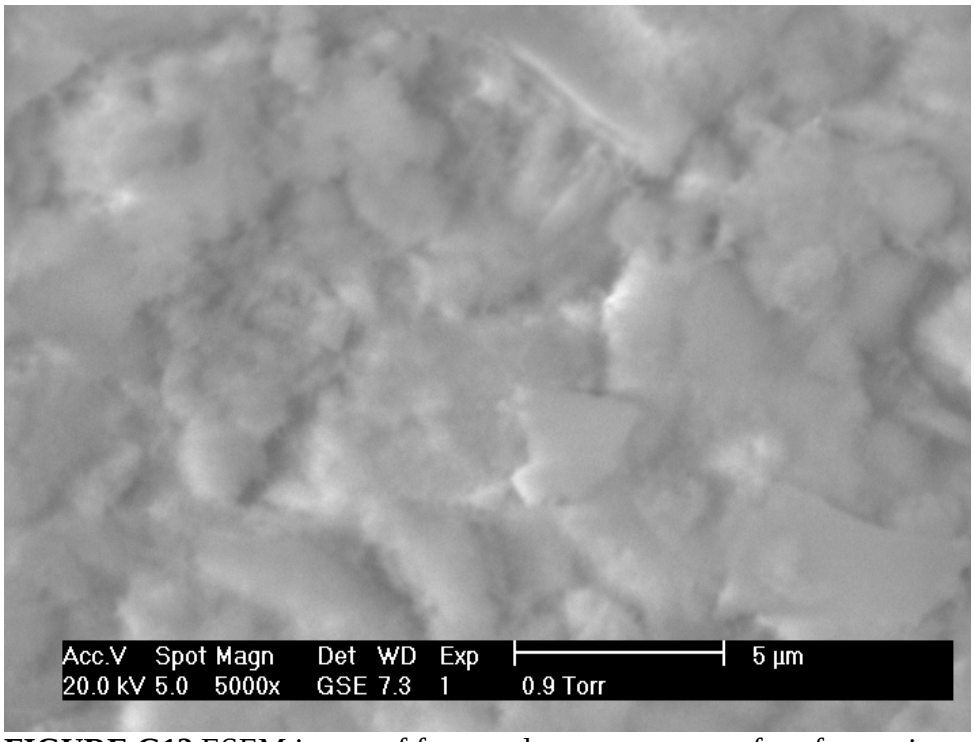


FIGURE G12 ESEM image of fractured cement paste surface from mixture C73 after 1 hour of hydration

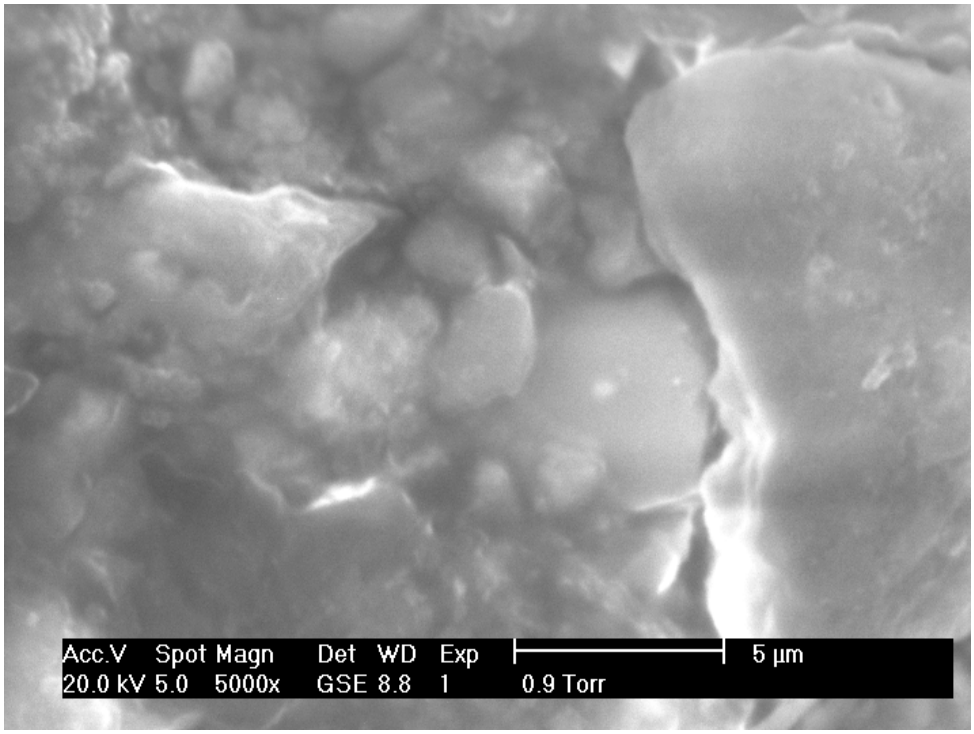


FIGURE G13 ESEM image of fractured cement paste surface from mixture C73 after 4 hours of hydration

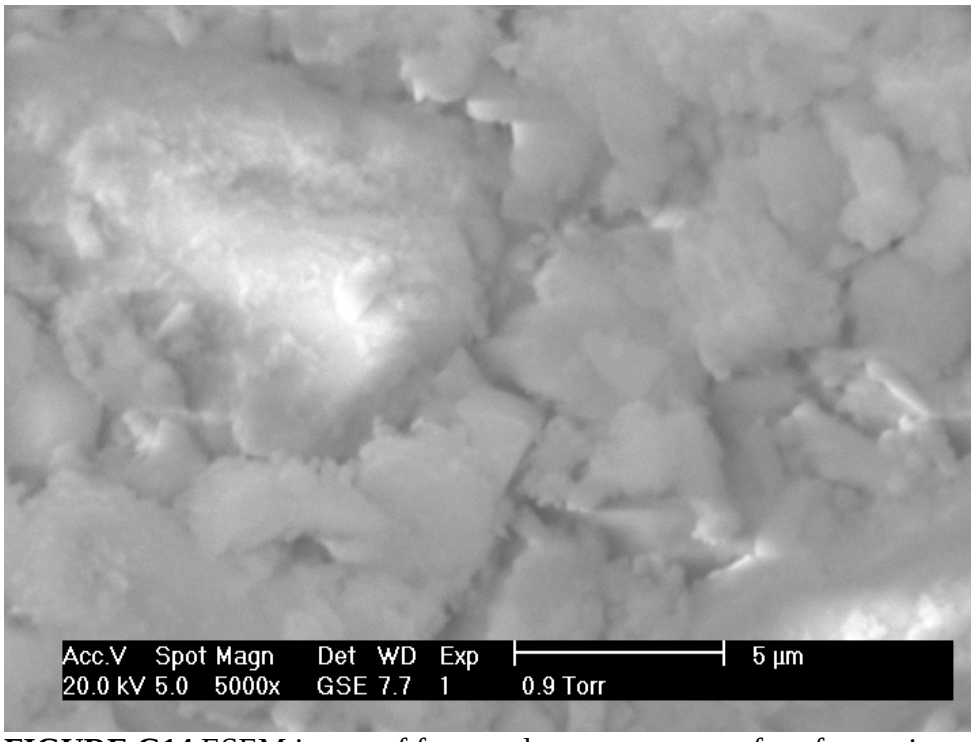


FIGURE G14 ESEM image of fractured cement paste surface from mixture LN73-00 after 1 hour of hydration

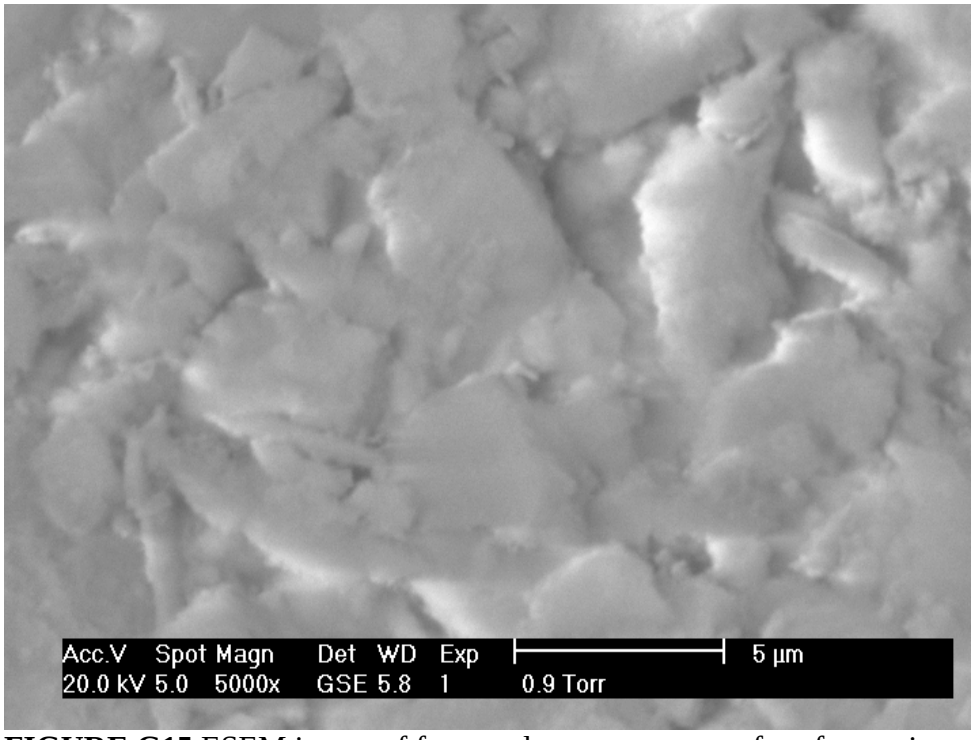


FIGURE G15 ESEM image of fractured cement paste surface from mixture LN73-00 after 4 hours of hydration

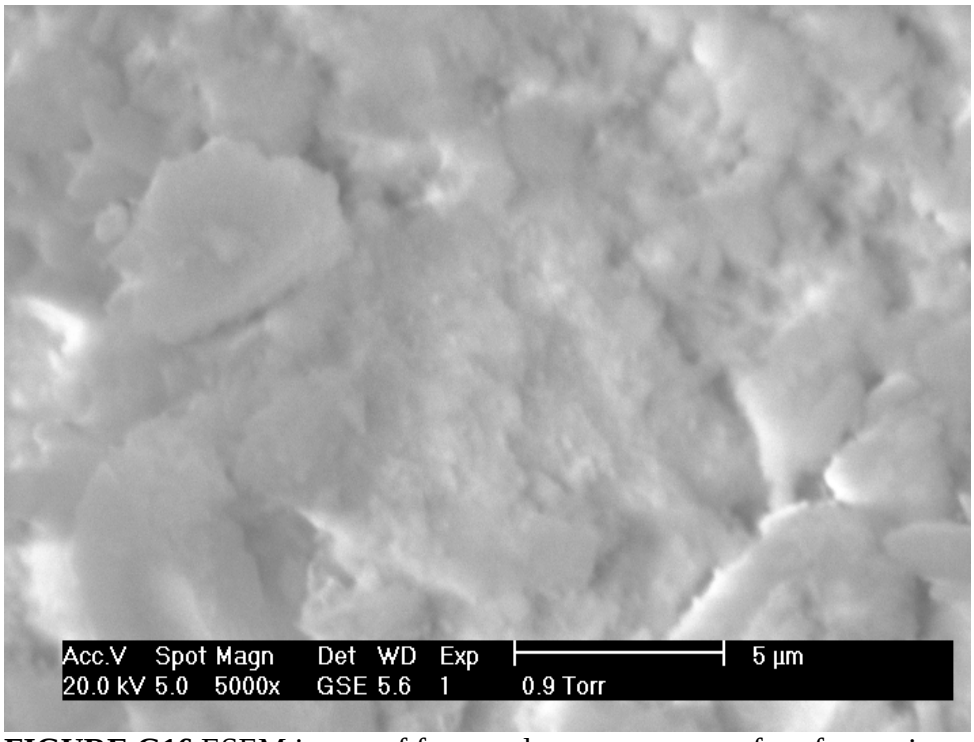


FIGURE G16 ESEM image of fractured cement paste surface from mixture LN73-105 after 1 hour of hydration

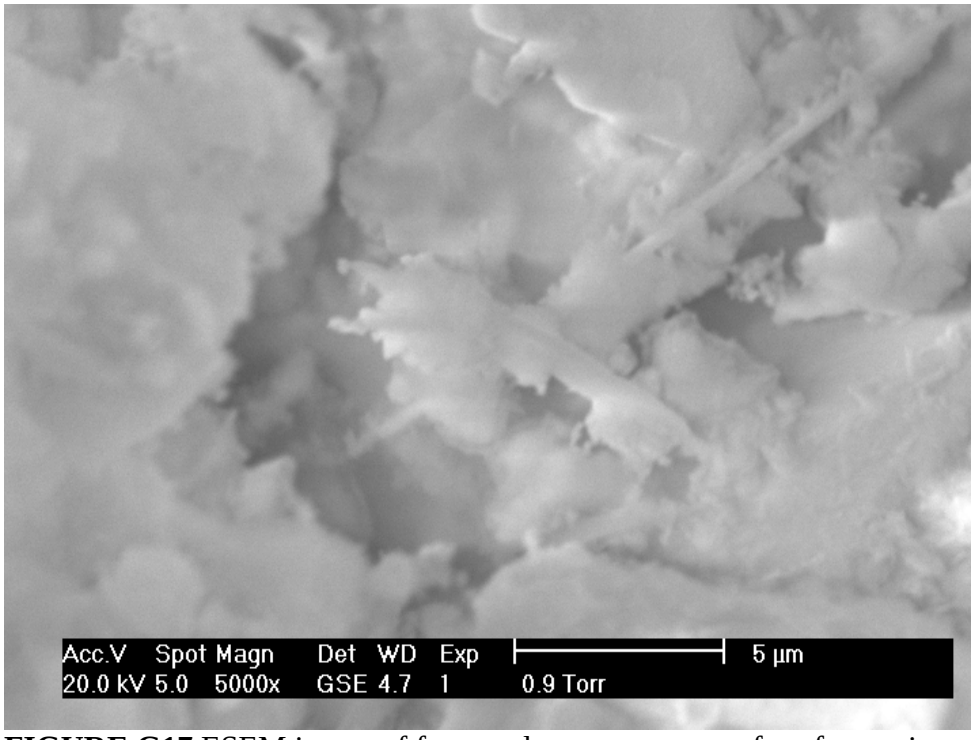


FIGURE G17 ESEM image of fractured cement paste surface from mixture LN73-105 after 4 hours of hydration

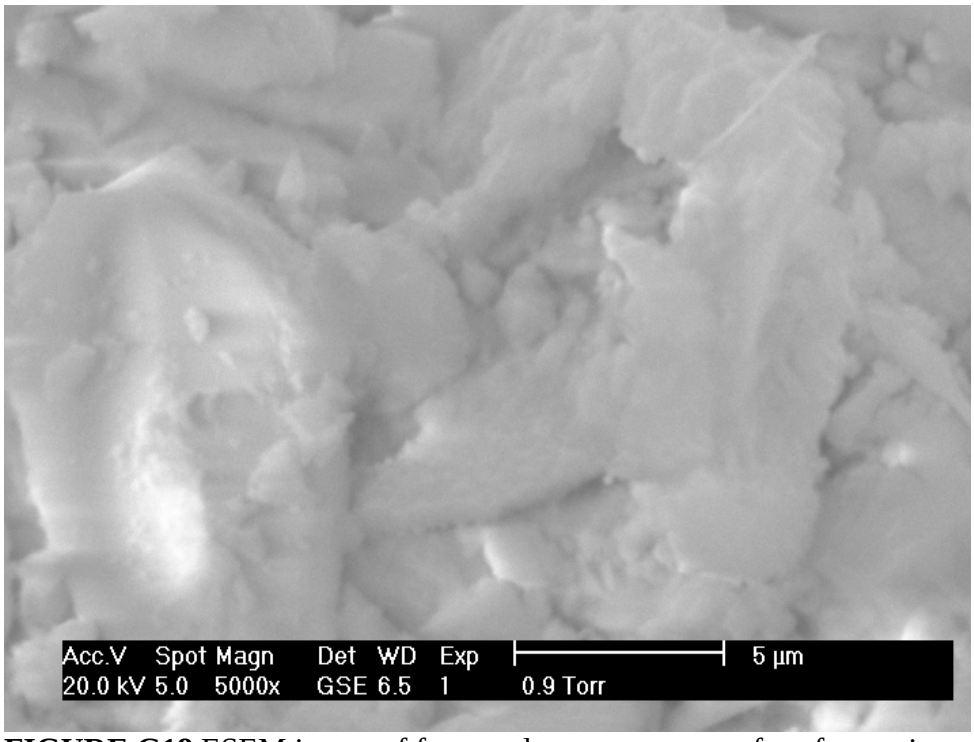


FIGURE G18 ESEM image of fractured cement paste surface from mixture LN50-00 after 1 hour of hydration

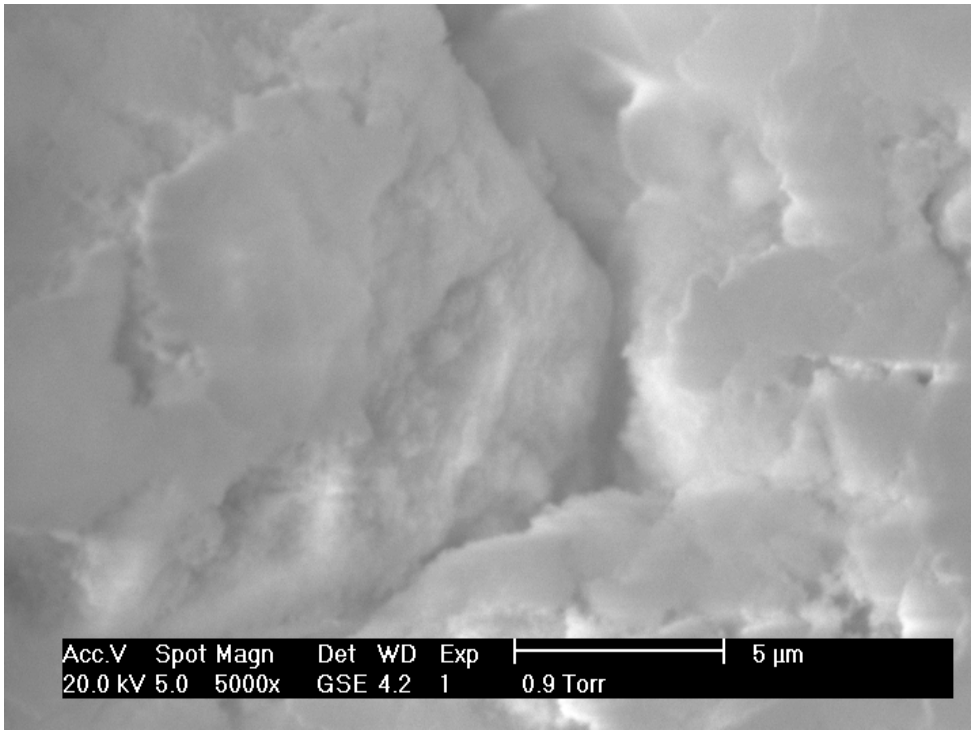


FIGURE G19 ESEM image of fractured cement paste surface from mixture LN50-00 after 4 hours of hydration

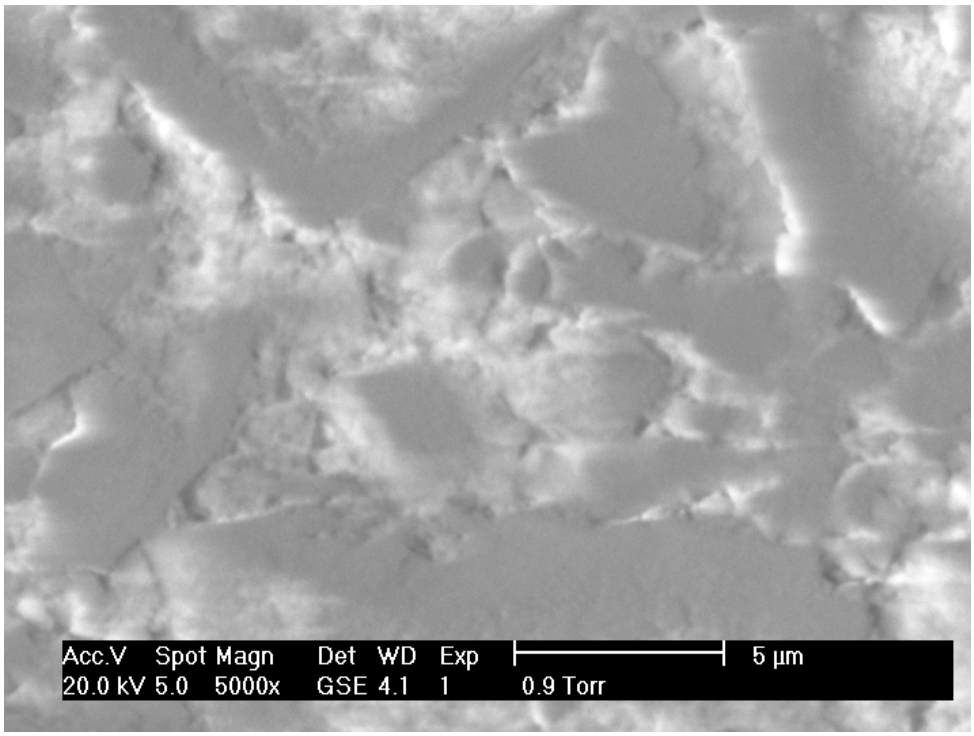


FIGURE G20 ESEM image of fractured cement paste surface from mixture LN32-00 after 1 hour of hydration

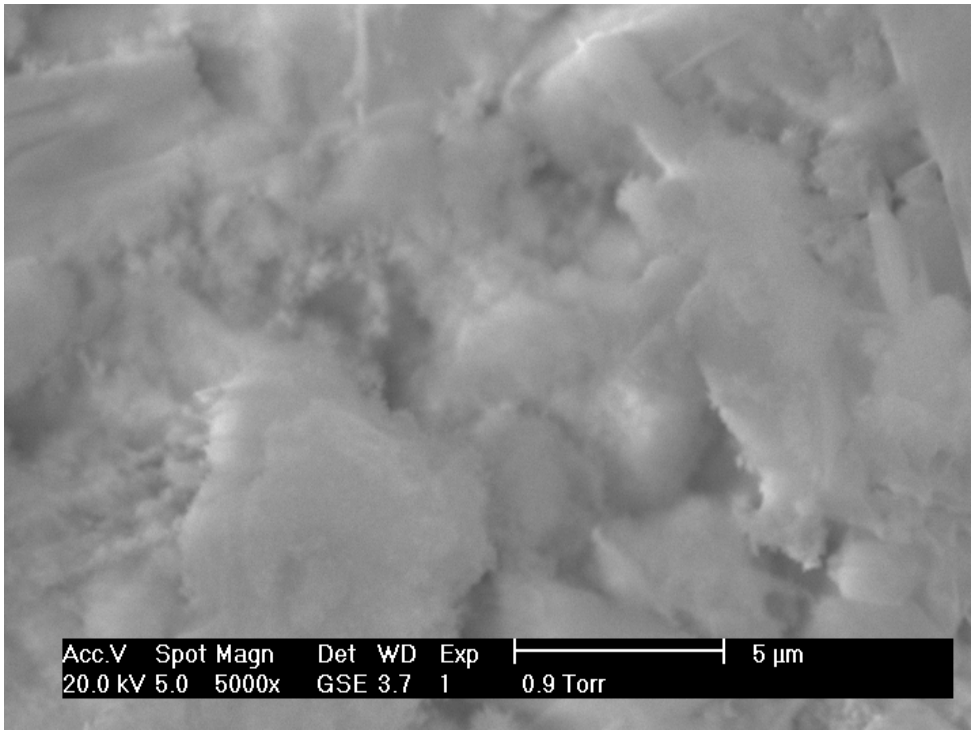


FIGURE G21 ESEM image of fractured cement paste surface from mixture LN32-00 after 4 hours of hydration

APPENDIX H: 1- and 7-day Compressive Strength Results for Delayed Dosing Concrete Mixtures

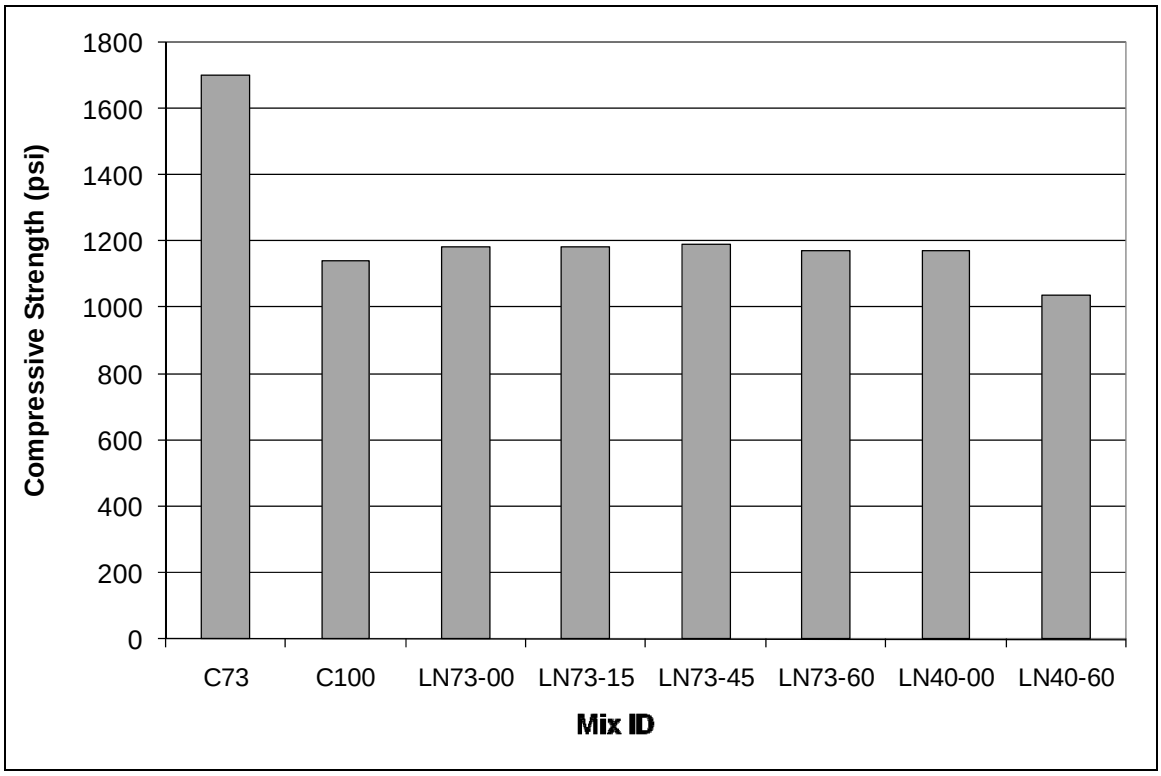


FIGURE H1 1-day compressive strengths for delayed dosing concrete mixtures

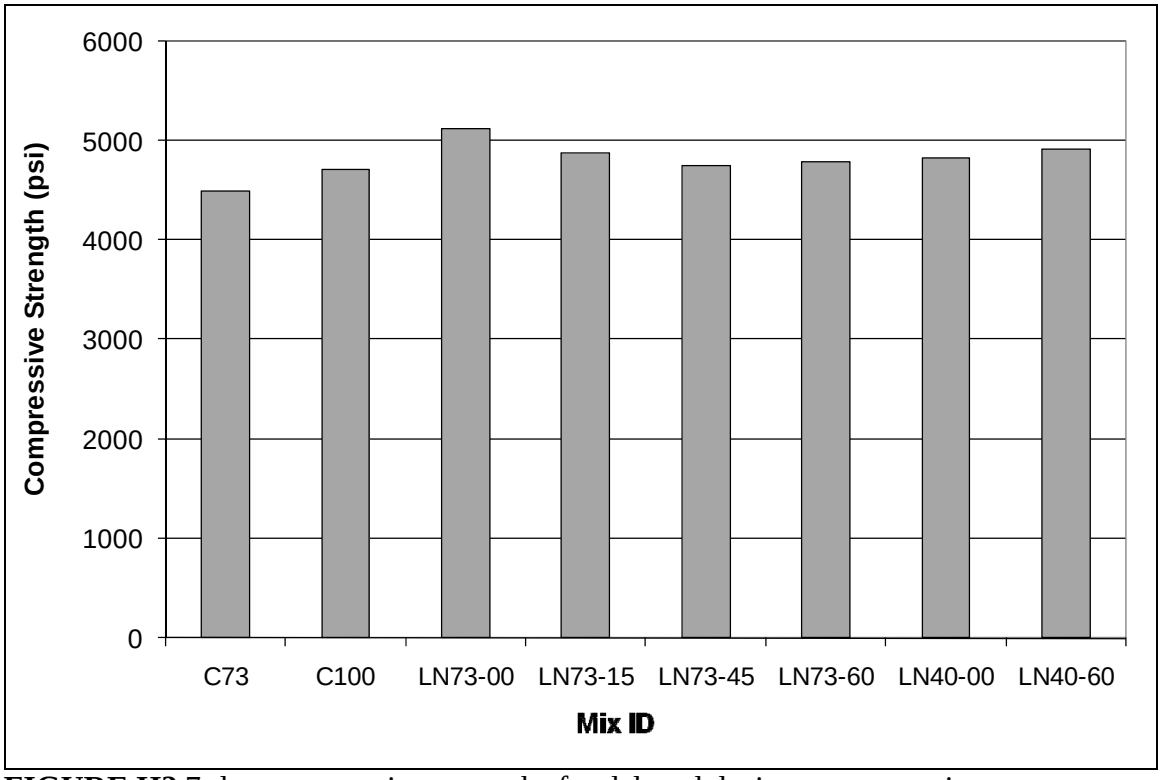


FIGURE H2 7-day compressive strengths for delayed dosing concrete mixtures

APPENDIX I: Temperature of Concrete Mixing Drums during Liquid Nitrogen Application

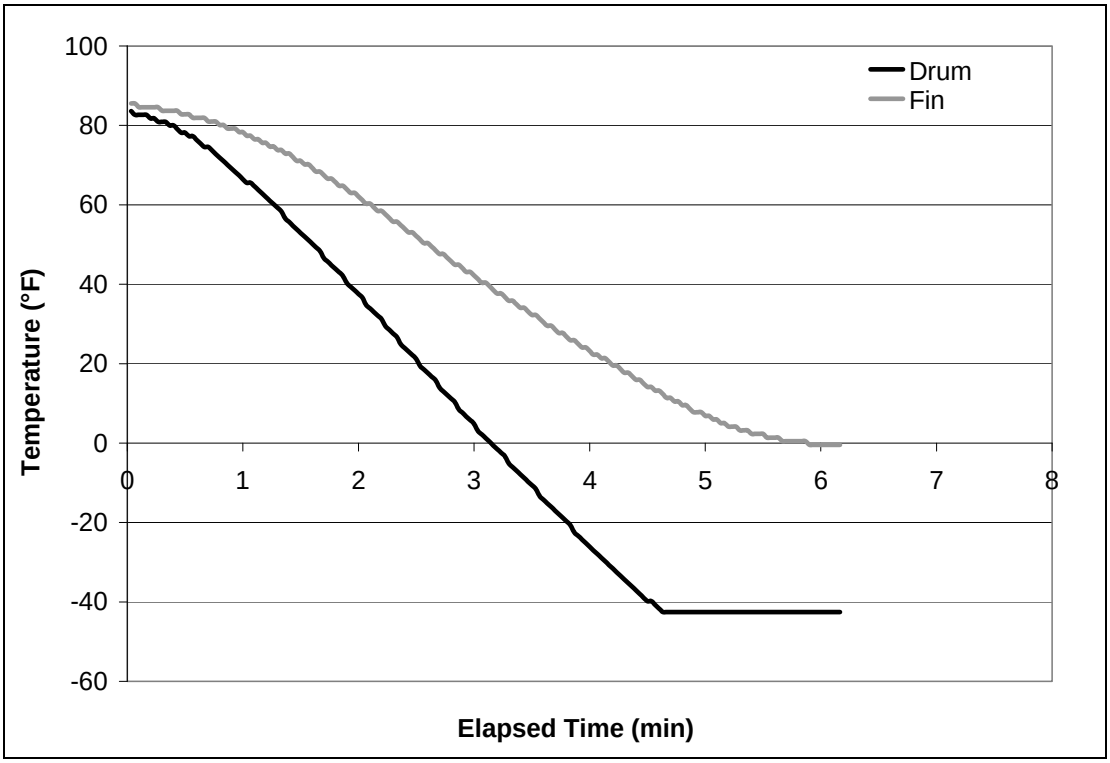


FIGURE I1 Temperature of mixing drum and fin during liquid nitrogen dosing (Truck 1)
Note: -40°F is the minimum temperature that can be recorded by the instrument

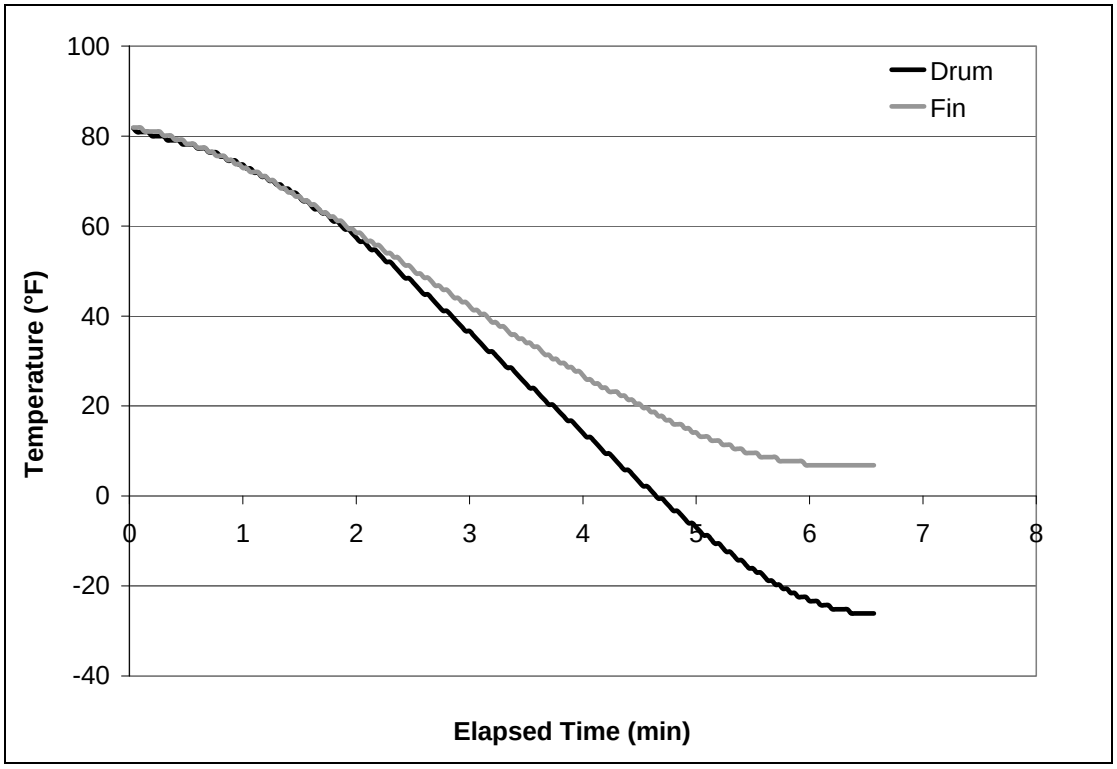


FIGURE I2 Temperature of mixing drum and fin during liquid nitrogen dosing (Truck 2)

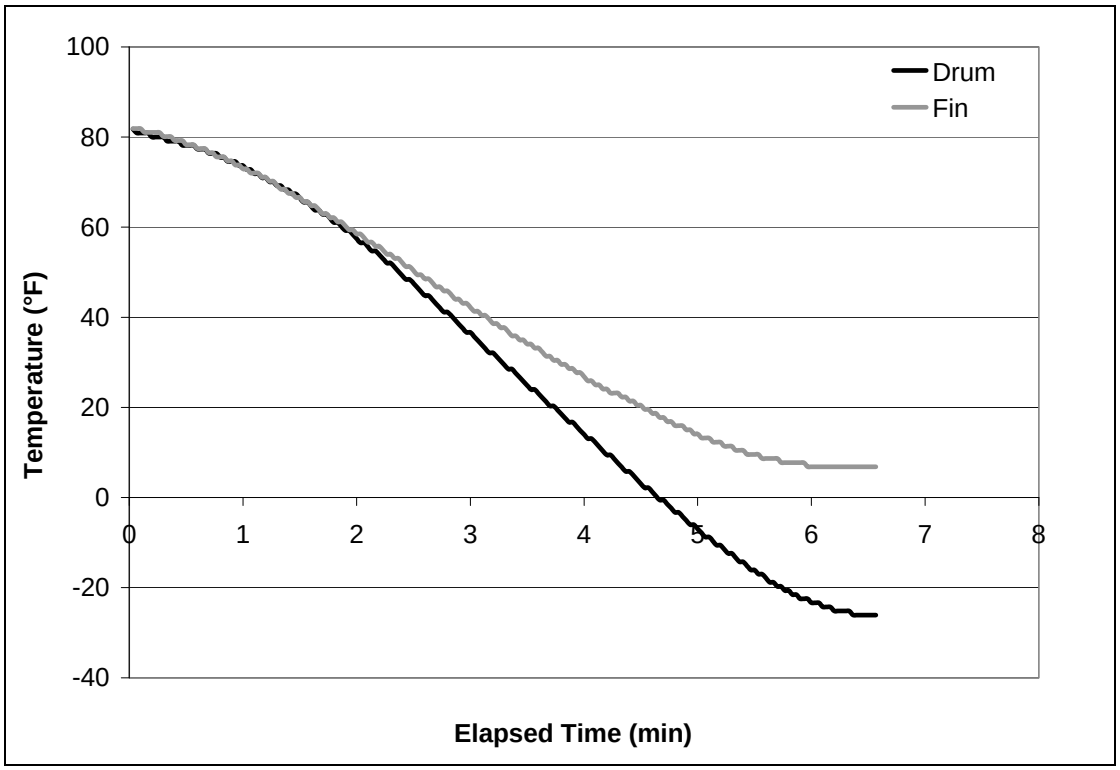


FIGURE I3 Temperature of mixing drum and fin during liquid nitrogen dosing (Truck 3)

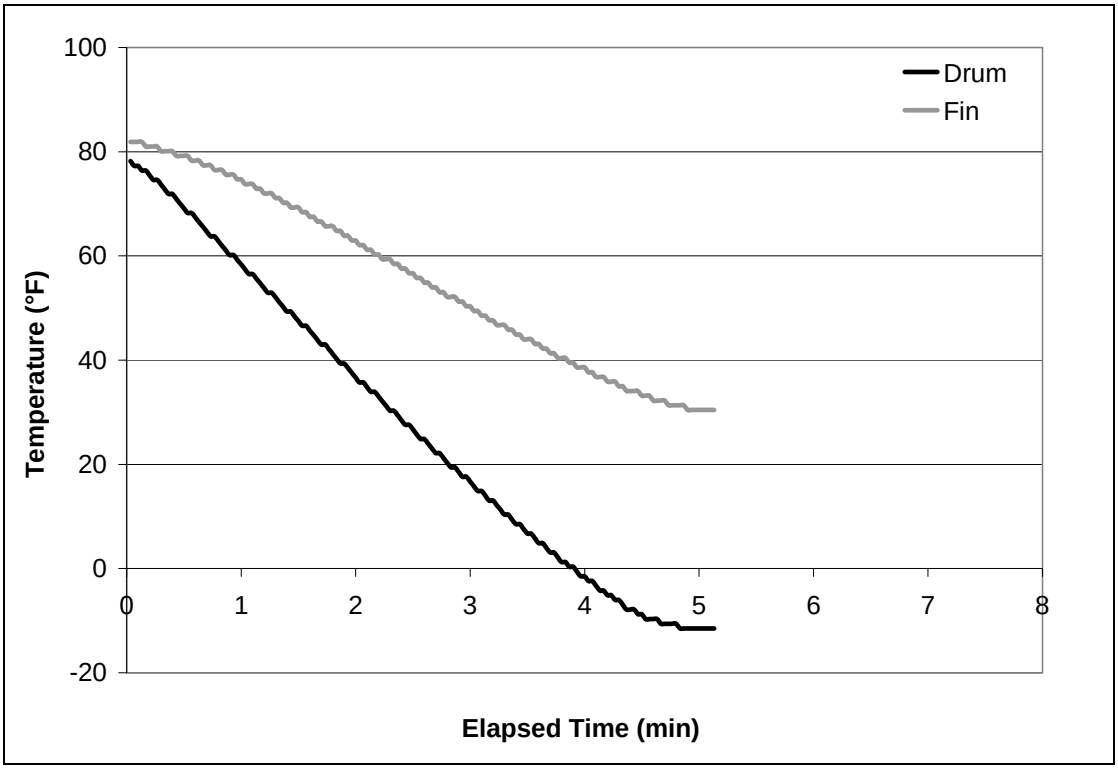


FIGURE I4 Temperature of mixing drum and fin during liquid nitrogen dosing (Truck 4)

REFERENCES

ACI Committee 116, Cement and Concrete Technology, *American Concrete Institute*, Farmington Hills, Michigan, 2000.

ACI Committee 207, Mass Concrete, *American Concrete Institute*, Farmington Hills, Michigan, 1996.

ACI Committee 301, Specifications for Structural Concrete, *American Concrete Institute*, Farmington Hills, Michigan, 1999.

ACI Committee 305, Hot-Weather Concreting, *American Concrete Institute*, Farmington Hills, Michigan, 1999.

ACI Committee 318, Building Code Requirements for Reinforced Concrete, *American Concrete Institute*, Farmington Hills, Michigan, 2005.

ASTM C 31, Standard Practice for Making and Curing Concrete Test Specimens in the Field, *ASTM International*, West Conshohocken, PA, 2003.

ASTM C 33, Standard Specification for Concrete Aggregates, *ASTM International*, West Conshohocken, PA, 2003.

ASTM C 39, Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens, *ASTM International*, West Conshohocken, PA, 2004.

ASTM C 109, Standard Test Method for Compressive Strength of Hydraulic Cement Mortars, *ASTM International*, West Conshohocken, PA, 2005.

ASTM C 138, Standard Test Method for Density (Unit Weight), Yield, and Air Content (Gravimetric) of Concrete, *ASTM International*, West Conshohocken, PA, 2001.

ASTM C 143, Standard Test Method for Slump of Hydraulic Cement Concrete, *ASTM International*, West Conshohocken, PA, 2003.

ASTM C 231, Standard Test Method for Air Content of Freshly Mixed Concrete by the Pressure Method, *ASTM International*, West Conshohocken, PA, 2004.

ASTM C 305, Standard Practice for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency, *ASTM International*, West Conshohocken, PA, 1999.

ASTM C 403, Standard Test Method for Time of Setting of Concrete Mixtures by Penetration Resistance, *ASTM International*, West Conshohocken, PA, 1999.

ASTM C 457, Standard Test Method for Microscopical Determination of Parameters of the Air-Void System in Hardened Concrete, *ASTM International*, West Conshohocken, PA, 1998.

ASTM C 469, Standard Test Method for Static Modulus of Elasticity and Poisson's Ratio of Concrete in Compression, *ASTM International*, West Conshohocken, PA, 2002.

ASTM C 496, Standard Test Method for Splitting Tensile Strength of Cylindrical Concrete Specimens, *ASTM International*, West Conshohocken, PA, 2004.

ASTM C 618, Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete, *ASTM International*, West Conshohocken, PA, 2005.

ASTM C 1202, Electrical Indication of Concrete's Ability to Resist Chloride Ion Penetration, *ASTM International*, West Conshohocken, PA, 1997.

ASTM C 1437, Standard Test Method for Flow of Hydraulic Cement Mortar, *ASTM International*, West Conshohocken, PA, 2001.

Atkins, H. N. Highway Materials, Soils, and Concretes, Fourth Edition. Prentice Hall, Upper Saddle River, NJ, 2003.

Blackwood, D., Hathaway, J., Paskevich, V., Poppe, L., "A Laboratory Manual for X-Ray Powder Diffraction," Report No. 01-141, United States Geological Survey, Reston, VA, 2001.

Boss, C.B., Freeden, K., Concepts, Instrumentation and Technique for Inductively Coupled Plasma Optical Emission Spectroscopy, 2nd edition, Perkin Elmer, 1997.

Burg, R.G., *The Influence of Casting and Curing Temperature on the Properties of Fresh and Hardened Concrete*, Portland Cement Association, Skokie, IL, 1996.

Chini, A.R., L.C. Muszynski, L. Acquaye, and S. Tarkhan, Determination of the Maximum Placement and Curing Temperatures in Mass Concrete to Avoid Durability Problems and DEF, Florida Department of Transportation Contract BC 354-29, 2003.

Escalante-Garcia, J.I., Sharp, J.H., "Effect of Temperature on the Hydration of the Main Clinker Phases in Portland Cements: Part I, Neat Cements," *Cement and Concrete Research*, volume 28, issue 9, 1998.

Hall, J.D., “Laboratory and Field Investigations of Alkali-Silica Reaction and its Interaction with Delayed Ettringite Formation,” Master’s Thesis, The University of Texas at Austin, Austin, Texas 2003.

Ichimura, A., Manning, B., "Bruker D8 ADVANCE Powder XRD Instrument Manual and Standard Operating Procedure (SOP)," San Francisco State University, August 2004. Accessed January 2007. http://funnel.sfsu.edu/xrd/documentation/Part%201_General%20Info_web.doc.

Idorn, G.M., “Hydration of Portland Cement Paste at High Temperature under Atmospheric Pressure,” *Proceedings of the 5th International Congress on the Chemistry of Cement*, 1969.

Johnson, Joe Dan, Personal Communication, Transit Mix Concrete and Materials Company, Austin, TX, 2006.

Kjellsen, K.O., Detwiler, R.J., Reaction-Kinetics of Portland Cement Mortars Hydrated at Different Temperatures, *Cement and Concrete Research*, volume 22, issue 1, 1992.

Kjellsen, K.O., “Heat Curing and Post-Heat Curing Regimes of High-Performance Concrete: Influence on Microstructure and C-S-H Composition,” *Cement and Concrete Research*, volume 26, issue 2, 1996.

Komonen J., Penttala, V., “Effects of High Temperature on the Pore Structure and Strength of Plain and Polypropylene Fiber Reinforced Cement Pastes,” *Fire Technology*, volume 39, number 1, 2003.

Kurita, M., Goto, S., Minegishi, K., Negami, Y., and Kuwahara, T., "Precooling Concrete Using Frozen Sand," *Concrete International*, volume 12, number 6, 1990.

Lee, M., "Economical Cooling of Hot Weather Concrete," *Concrete Construction*, volume 9, 1989.

Lerch, W., “Hot Cement and Hot Weather Concrete Tests,” Portland Cement Association, Skokie, IL, 1955.

Malisch, W., "Comparing the Options for Cooling Concrete," *Concrete Producer*, volume 15, number 5, pp. 317-320, 1997.

Mindess, S., Young, J.F., and Darwin, D., *Concrete*, Prentice Hall, New Jersey, 2003.

Nakahara, Y., Yurugi, M., Nikaido, M., Shiraishi, Y., "Cooling of Dam Concrete Mixtures with Liquid Nitrogen," Transactions of the Japan Concrete Institute, volume 9, 1987.

Nakane, S., Saito, H., Ohike, T., Strength Development and Microstructure of Cement and Concrete Precooled with Liquid Nitrogen, Proceedings of the International Conference on Concrete in Hot Climates, *Concrete in Hot Climates*, 1992.

Neubauer, C.M. Jennings, H.M., "The Role of the Environmental Scanning Electron Microscope in the Investigation in Cement Based Materials," *Scanning*, volume 18, issue 7, 1996.

PCA IS177, *Concrete Slab Surface Defects: Causes, Prevention, Repair*, Portland Cement Association, Skokie, IL, 2001.

Poole, J.L., Riding, K.A., Folliard, K.J., Juenger, M.C.G. and A.K. Schindler, "Hydration study of cementitious materials using semi-adiabatic calorimetry," *Concrete Heat Development: Monitoring, Prediction, and Management*, eds. K. Wang and A.K. Schindler, S.P. 241-CD, American Concrete Institute, Farmington Hills, MI, 2007.

Price, W.H., "Factors Influencing Concrete Strength," *Journal of the American Concrete Institute*, volume 47, 1951.

Robinson, S. J., "How ESEM Works," Imaging Technology Group, Urbana, IL, 2003. http://www.itg.uiuc.edu/ms/equipment/microscopes/esem/how_it_works.htm. Accessed January 2007.

Schields, P.J., "Bragg's Law and Diffraction: How waves reveal the atomic structure of crystals," Center for High Pressure Research, State University of New York at Stony Brook, 2004. http://www.eserc.stonybrook.edu/ProjectJava/Bragg/. Accessed January 2007.

Schindler, A.K., Folliard, K.J., "Heat of Hydration Models for Cementitious Materials," *ACI Materials Journal*, volume 102, number 1, 2005.

Scrivener, K.L., T. Füllmann, E. Gallucci, G. Walenta, and E. Bermejo, "Quantitative Study of Portland Cement Hydration by X-Ray Diffraction/Rietveld Analysis and Independent Methods", *Cement and Concrete Research*, volume 34, 2004.

Solt, S.M., "Liquid Nitrogen for Cooling Concrete: Safety Precautions, Methods of Injection, and Effects on Setting Time and Drying Shrinkage," M.S. Thesis, The University of Texas at Austin, Austin, Texas 2006.

Taylor, P.C., Kosmatka, S.H., Voigt, G.F., *Integrated Materials and Construction Practices for Concrete Pavement: A State-of-the-Practice Manual*, Federal Highway Administration, FHWA Report No.: HIF - 07 – 004, December 2006.

TxDOT, Specification 420 - Standard Specifications for Construction of Highways, Streets and Bridges, Texas Department of Transportation, 2004.

Wang, K., Ge, Z., Grove, J., Mauricio Ruiz, J., Rasmussen, R., Ferragut, T., "Developing a Simple and Rapid Test for Monitoring the Heat Evolution of Concrete Mixtures for Both Laboratory and Field Applications," FHWA DTF61-01-00042, Iowa State University, Ames, IA, 2007.

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